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ELEMENTS OF CHEMISTRY

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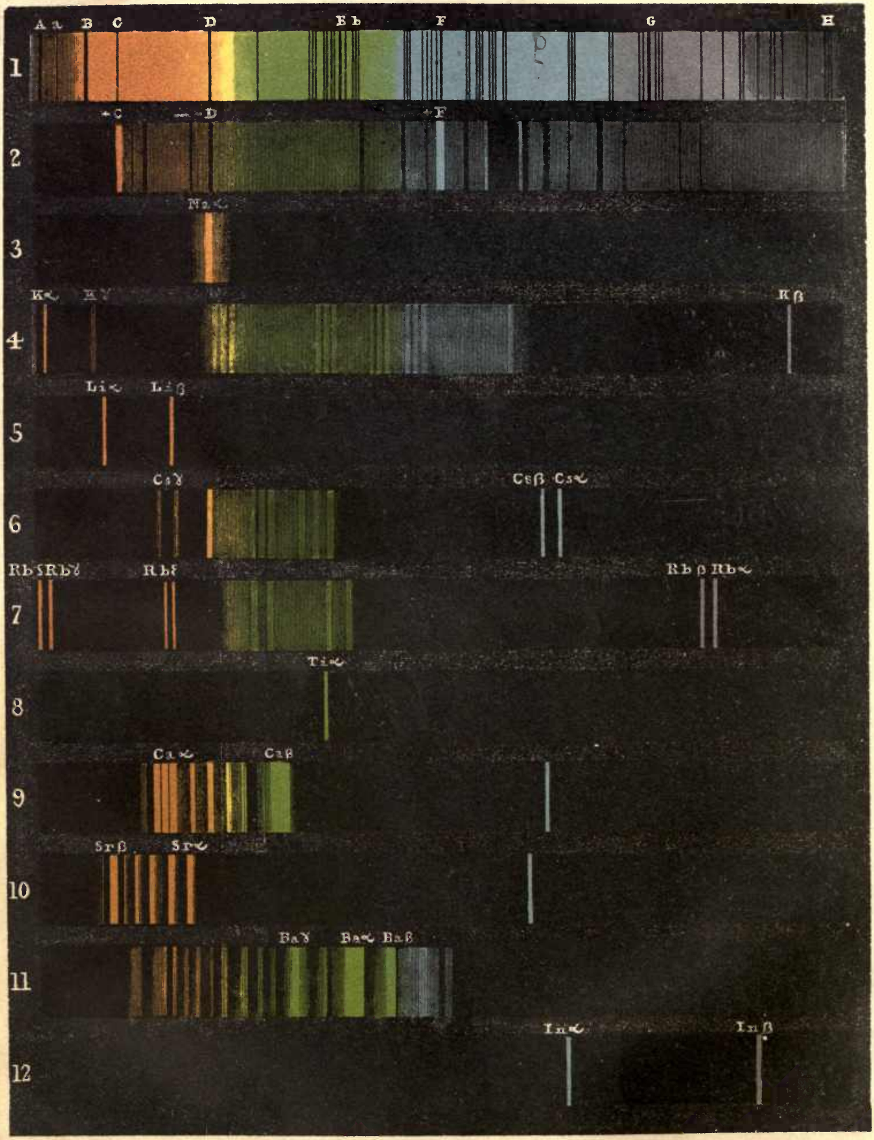
CHEMISTRY.

SPECTRA OF VARIOUS SOURCES OF LIGHT.



1. *The Sun.* 2. *The Sun's edge.* 3. *Sodium.* 4. *Potassium.* 5. *Lithium.* 6. *Caesium.* 7. *Rubidium.* 8 *Thallium.* 9. *Calcium.* 10. *Strontium.* 11. *Barium.* 12. *Indium.*

Appletons' Science Text-Books.

THE

ELEMENTS OF CHEMISTRY.

BY

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PREFACE.

In preparing this little treatise the author has had several objects in view. First, he has sought to write a text-book which should be available for use with elementary classes, and in which the difficulties of chemical science should be encountered progressively, rather than at the beginning. Secondly, he has considered the needs of those students who, while anxious to learn, are unable to secure the aid of a teacher, and who, therefore, are obliged to study by themselves. For the latter, especially, are the foot-note references to other works on chemistry; and only such works have been cited as are to be found on the shelves of nearly every well-equipped public library. He has also borne steadily in mind the fact that in most schools there are two classes of students: those who study chemistry merely as part of a general education, without thought of going further; and those who are likely in time to take a more advanced course of chemical training. For the former class the book is sufficiently full, particularly with regard to the everyday applications of chemistry; for the second class it is intended to serve as a legitimate scientific basis for subsequent higher study.

The value of a school text-book, other things being equal, depends much upon the use made of it by the teacher. In his hands it may become an instrument for developing thought, or merely a device for drilling the memory. This is especially true of text-books upon chemistry. To use them properly it must always be remembered that chemistry is essentially a disciplinary study—as much so as language or mathematics; and the constant effort of the teacher should be to train the pupil in the accurate observation of phenomena, and the ability to draw correct conclusions from what he sees. Good discipline in scientific methods of thought must always be kept in view; and this discipline can be best attained by simultaneous drill in the facts of science as observed in the lecture-room or laboratory, and in the philosophy of science which is reared upon them. In this book the effort has been made to present, as a rule, experimental evidence first and theoretical discussions afterward; and a glance at the chapters upon atomic weights, formulæ, and valency, will fairly illustrate the manner in which this purpose has been carried out.

Nearly all the experiments cited in this volume are of the simplest character. The greater number of them can be easily performed by the pupil himself, with no more complicated apparatus than can be improvised from such common materials as are everywhere at hand. The chemicals, with few exceptions, are inexpensive, and within the reach of every school; and, although a good laboratory is desirable, it is not necessary to the attainment of really substantial results. Every experiment should be studied, not as an amusement, but for what it signifies; and, if there are not means for performing it just as it is described, other means may be readily devised. The student who constructs his own apparatus understands its meaning much better than if he had bought a far more elegant outfit of some dealer.

The questions and exercises at the end of the book are not meant to be exhaustive. They are merely hints to aid both teacher and pupil in their work. The problems, in particular, are only tentative; some classes will need many more than are given, and the teacher must devise such as will be best suited to circumstances.

The author's acknowledgments are due to Miss Caroline A. Lord, of Cincinnati, for efficient service in the preparation of a considerable number of the illustrations.

WASHINGTON, *April*, 1884.

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PART I.

INORGANIC CHEMISTRY.

CHAPTER I.

INTRODUCTION.

WHEN we closely observe the occurrences of Nature, we soon see that two great classes of changes are constantly taking place. First, there are the changes which do not affect the essential character of things: like the motion of a body from one spot to another, and the variations between heat and cold, sound and silence, light and darkness, and so on. Secondly, there are the changes which substances undergo in their innermost structure: like the transformation of wood into charcoal, of the constituents of soil and air into the stems and leaves of plants, and a multitude of other similar alterations of different degrees of complexity. Changes of the first class are called physical changes, while the others are known as chemical; and it is with the latter that the science of chemistry has to do.

For example, a piece of iron may be converted into a magnet and afterward deprived of its magnetic power, thus acquiring and losing a certain new property without ceasing to be metallic iron. These changes, which do not affect the nature of the metal as a metal, are physical; and so also are those involved in raising a piece of the iron to a red heat, or in rendering it fluid by melting. But if the iron be placed in a shallow pool of water, so as to be partly covered and partly exposed to the air, it will be slowly transformed into a brownish-red substance called rust, and here the alteration is chemical. The iron has ceased to exist as iron, and has become changed into something quite different. Again, water may be frozen into ice, or converted by heat into steam; thus showing its capacity to exist in several different conditions, without ceasing to be the same substance. These changes, therefore, are physical. But, by chemical means, the water may be decomposed into two gases—oxygen and hydrogen—each of which differs widely in its properties from water, and neither of which without the other can reproduce water. This transformation of water into something else is a chemical transformation.

The following experiments will serve to illustrate chemical changes:

Experiment 1.—Rub together in a mortar a small quantity of copper-filings with half their weight of sulphur. No matter how thoroughly you mix them, you can still, with a magnifying-glass, discern the separate particles of the two substances. Now insert the mixture in a glass tube sealed at the lower end, and heat gently over a flame. Presently the sulphur will melt, and shortly afterward the entire mass will become incandescent. Upon cooling, it will be found that both copper and sulphur have disappeared, and in their place is a grayish substance, in which the most powerful microscope can detect no particle of either of the original bodies. The copper and sulphur have united to form a new substance, known as copper sulphide; and thus the experiment serves to illustrate *chemical combination*. It also teaches the difference between chemical combination and mere mechanical mixture. Instead of copper, iron may be used in this experiment, and then iron sulphide will be formed. Before heating, the metal may be separated from the sulphur by means of a magnet; but after union has taken place the iron can not be thus withdrawn.

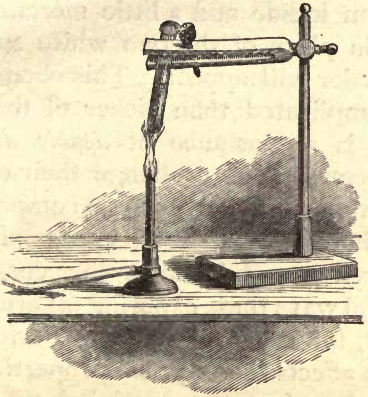

FIG. 1.—Union by Heat.

EXPERIMENT 2.—Place in a dry test-tube a little red mercuric oxide, and heat cautiously over a flame. Soon globules of metallic mercury or quicksilver will be seen in the bottom of the tube, or condensed upon its cooler sides. In the tube there will also be a quantity of oxygen gas, which may be recognized by the fact that a kindled match will burn more brilliantly in it than in the outer air.

The original red substance has been divided into two substances, a gas and a metal; so that here we have an instance of *chemical decomposition.**

EXPERIMENT 3.—Rub together in a mortar a little potassium iodide and a little mercuric chloride. Presently, in place of the two white substances, a scarlet powder will appear. This chemical change is more complicated than either of the foregoing cases, and is an instance of *double decomposition.* Here two compounds exchange their constituents, each decomposing the other, new compounds at the same time being formed. This phase of action will be considered more fully in another chapter.

In several ways these experiments are instructive. They show, for example, how wonderfully a chemical change affects the physical properties of things, the properties of a compound being often widely different from those of the substances which have united to produce it. Under proper conditions, black, tasteless, odorless charcoal may be made to unite with yellow, tasteless, odorless sulphur; the product of the union of these two solids being a volatile, colorless, transparent liquid, with a nauseous odor and burning taste. A more complete transformation can hardly be imagined.†

It will be observed that in two of the foregoing

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* Copper formate is even better than mercuric oxide for strikingly illustrating decomposition. When heated in a tube the brilliant blue crystals evolve gas copiously, and pure metallic copper remains behind. The substance may be prepared by dissolving copper oxide in warm formic acid, and allowing the solution to crystallize. Unfortunately, the materials are not readily available in all school laboratories.

† At this point the teacher will do well to show the class, side by side, a fragment of charcoal, a bit of sulphur, and a bottle of carbon disulphide.

experiments heat is applied: in one case as a decomposing agent, in the other as a means of causing union. Another experiment will bear advantageously upon these.

EXPERIMENT 4.—Pulverize, in a *perfectly clean mortar*, a little potassium chlorate. Transfer it to a sheet of paper, and mix carefully with it, *without rubbing*, an equal quantity of powdered sugar. Place the mixture where no harm can be done, and drop upon it, from a glass rod, a single drop of strong sulphuric acid. The mass will immediately catch fire, burning with almost explosive violence, and with a peculiar rose-colored flame. Here, then, we have a chemical change which *produces* a great amount of heat.

We now see that *heat* plays a very important part in chemical changes; and, as we go on, we shall find that other agencies, such as light, electricity, etc., are also often involved. In order, then, that a chemical change may be completely understood, three things have to be studied, as follows:

First, the properties of the substances entering into the change. *Secondly*, the physical phenomena occurring during the change. *Thirdly*, the properties of the substances which result from the change.

In such investigations one principle, which underlies all science, must be steadily kept in view. *In no case is anything, either matter or force, ever created or destroyed.* By *matter* is meant anything which occupies space and possesses weight: like iron, wood, water, or air. By *force* is understood any agency capable of producing motion, or of altering the direction of a moving body;* and such things as heat, light, electricity, mechanical power, etc., are called forces. When two bodies act upon each other chemically, they do so under the influence of a peculiar force, known variously as chemical affinity, chemical attraction, or, more briefly, chemism. When two substances unite, it is this force which brings them together; when they are separated, this force has to be overcome. In consequence, every chemical change involves some transformation of force, but none is ever created or destroyed. So also with the matter changed: however complicated its alteration may be, no particle is ever lost, no new particle ever appears. When a candle is burned, a series of chemical changes takes place. Heat is developed by chemical action, and a certain amount of matter seems to disappear. But, if all the products of combustion, solid or gaseous, be collected and accurately weighed, it will be found that nothing has really vanished. The matter of the candle and of the air in which it burned have acted upon each other chemically, and new substances have been formed; but neither destruction nor creation of matter was possible. It is with the transformations of matter, its *combinations* and *decompositions*, that the chemist has to deal.

In the light of the foregoing pages we may now frame an intelligible definition, as follows: *Chemistry is the science which investigates the composition of substances, together with the combinations and decompositions resulting from their action upon one another under the influence of chemical force.*†

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* For more exhaustive definitions, the works on mechanics and physics may be consulted.

† The essential features of this definition may be expressed in a

At the beginning of any study the question of utility is apt to arise. With chemistry the answer to this question is twofold: First, its value as an educational instrument, as a means of mental discipline, is very great. Secondly, its material advantages are enormous. The discoveries of chemists are now applied to practical use in agriculture, in medicine, and in every great manufacturing industry. By the help of chemistry many substances which were formerly wasted are now rendered useful. For example, from coal-tar the most brilliant dyes are made. Our dwellings are now lighted with chemically refined oil and candles, or by chemically made gas; and these are kindled with matches which chemistry has given us in place of the old flint and steel. Our clothing is bleached or dyed by chemical means; metals are extracted from their ores by chemical processes; soap, glass, porcelain, paints, varnishes, etc., have all become better and cheaper than before the chemist studied them. Barren soil is now rendered fruitful by chemical fertilizers; wood is preserved from decay by chemical applications; diseases are checked by chemical disinfectants; and a multitude of chemical preparations aid the physician in alleviating pain.

variety of other ways. The pupil will find it a useful exercise to arrange other definitions, so as to see the subject from several different points of view.

CHAPTER II.

THE CONSTITUTION OF MATTER.

In order to determine the composition of any substance, the chemist may resort to two distinct methods, *analysis* and *synthesis*. By analysis, a body is separated into its component parts, which are then identified. By synthesis these parts may be artificially combined, so as to produce the substance under investigation. For example, the composition of water may be ascertained by dividing it into its two constituents, oxygen and hydrogen; or it may be determined by causing these gases to unite, and proving that by their union water is actually formed. Each method re-enforces the other, and strengthens the final conclusion.

In Nature the chemist recognizes an almost limitless number of different substances, the composition of which he tries to discover by either or both of the above methods. Besides, he has to deal with vast numbers of artificial bodies; of which so many are theoretically possible that infinity would barely suffice to express them. In the analysis of all these substances, however, he finds the same component parts continually repeated in various modes of union; and he finally arrives at bodies so simple that they can not be analyzed further. These simple substances, of which at present some seventy are known, he terms *elements.* All other substances, which are formed by the chemical union of elements with each other, and which are consequently separable into elements by analysis, he calls *compounds.* Thus, the oxygen and hydrogen previously referred to are elements, for by no means within the chemist's control can they be decomposed into simpler bodies; while the water formed by their union is a compound, and is said to be composed of these elements. The following table contains a list of all the elements now known. The use of the "symbols" and the meaning of the "atomic weights" will be explained further on. New elements are occasionally discovered, usually as constituents of very rare minerals.

Table I.—Elements, Symbols, and Atomic Weights.

NAME.	Symbol.	Atomic weight.	NAME.	Symbol.	Atomic weight.
Aluminum	Al.	27.	Erbium	Er.	166.
Antimony	Sb.	120.	FLUORINE	F.	19.
ARSENIC	As.	75.	Gallium	Ga.	69.
Barium	Ba.	137.	Glucinum	Gl.	9.
Bismuth	Bi.	208.	Gold	Au.	196.5
BORON	B.	11.	HYDROGEN	H.	1.
BROMINE	Br.	80.	Indium	In.	113.6
Cadmium	Cd.	112.	IODINE	I.	127.
Cæsium	Cs.	133.	Iridium	Ir.	193.
Calcium	Ca.	40.	Iron	Fe.	56.
CARBON	C.	12.	Lanthanum	La.	138.2
CERIUM	Ce.	141.	Lead	Pb.	207.
CHLORINE	Cl.	35.5	Lithium	Li.	7.
Chromium	Cr.	52.	Magnesium	Mg.	24.
Cobalt	Co.	59.	Manganese	Mn.	55.
Columbium	Cb.	94.	Mercury	Hg.	200.
Copper	Cu.	63.3	Molybdenum	Mo.	96.
Decipium	Dp.	?	Nickel	Ni.	58.
Didymium	Di.	142.3	NITROGEN	N.	14.

NAME.	Symbol.	Atomic weight.	NAME.	Symbol.	Atomic weight.
Osmium	Os.	199. ?	SULPHUR	S.	32.
OXYGEN	O.	16.	Tantalum	Ta.	182.6
Palladium	Pd.	106.	TELLURIUM	Te.	126. ?
PHOSPHORUS	P.	31.	Terbium	Tb.	?
Platinum	Pt.	195.	Thallium	Tl.	204.
Potassium	K.	39.	Thorium	Th.	232.
Rhodium	Rh.	104.	Thulium	Tm.	?
Rubidium	Rb.	85.5	Tin	Sn.	118.
Ruthenium	Ru.	104.	Titanium	Ti.	48.
Samarium	Sm.	150.	Tungsten	W.	184.
Scandium	Sc.	44.	Uranium	U.	239.
SELENIUM	Se.	79.	Vanadium	V.	51.5
SILICON	Si.	28.	Yttrium	Yt.	89.
Silver	Ag.	108.	Ytterbium	Yb.	173.
Sodium	Na.	23.	Zinc	Zn.	65.
Strontium	Sr.	87.5	Zirconium	Zr.	90.

Of these elements by far the greater number are metallic; like gold, iron, zinc, etc. A smaller number, given in the table in small capitals, are called non-metallic; and of these carbon, oxygen, and sulphur are good examples. In the subsequent chapters the latter class of elements will be studied first. Between the metals and the non-metals, however, no sharp distinctions can be drawn; arsenic, for example, may be fairly put in either class; the division, therefore, is mainly one of convenience, and is not fundamentally important.

In order that we may be able to account for many of the properties of matter, we must study its physical constitution still more closely. Take, for example, a piece of iron: when it is heated, it expands, and occupies more space than before; when cooled, it contracts and becomes smaller; although in both cases the weight remains the same.

Weight, therefore, may be regarded a constant property of matter, while volume or bulk is variable. This variability in volume is most easily accounted for upon the supposition that matter, as we ordinarily recognize it, is made up of minute, separate particles, which may be driven farther apart or crowded closer together by various means. These particles the physicist terms *molecules*, and they are considered to be by all mechanical means indivisible. Every kind of matter is built up of its own characteristic kind of molecules; these are exactly alike, although different from the molecules of every other substance, and they are separated by larger or smaller spaces. They are furthermore supposed to be in more or less rapid motion; and upon this supposition the mathematical theories of heat and electricity are very largely based. Of course, molecules are exceedingly small—so small that we may never be able to see or handle them experimentally. There are, however, abundant reasons for asserting their existence; and it is even possible to calculate from physical data something approximate concerning their size. Evidence can be drawn from several sources showing that about five hundred millions of hydrogen-molecules, placed in a row, would only form a line an inch long; or, in other words, there are about two hundred millions to the linear centimetre.*

But, although molecules are mechanically indivisible, by chemical means we can divide them into smaller particles still. For example, a drop of water

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* For fuller details, consult Tait's "Recent Advances in Physical Science," chapters xii and xiii; also Cooke's "New Chemistry," pp. 27–36.

may be divided and subdivided until the molecules of water are reached; and each of these will still possess all the properties of water. But water is a compound of two elements, oxygen and hydrogen; and therefore every one of its molecules may be decomposed into these two substances. The smaller portions of oxygen and hydrogen thus recognized are called *atoms.* The molecule of any chemical compound, then, is a cluster of atoms; and it is only between atoms that the force of chemical attraction comes into play. In future chapters some of the properties of atoms will be considered. For present purposes the following definitions will be found useful:

A mass of matter is any portion of matter which can be recognized by the senses. Every mass is an aggregation of molecules. Masses attract each other by the force of gravitation. The science of mechanics deals with masses and their motions.

A molecule is the smallest particle of any substance which can exist in the free state, and in which the characteristic properties of the substance are retained. It is also the smallest portion of matter which can take part in any physical change. The science of molecular physics (including heat, light, and electricity) deals largely with molecules and their motions. Nearly all molecules are clusters of atoms; but, for a very few substances, the molecule and the atom are the same.

An atom is the smallest quantity of any substance which can enter into chemical union, or take part in any chemical change. Chemistry may be defined as the science which treats of atoms and their attractions for each other.*

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* This definition may be considered as a supplement to the one given in the preceding chapter. The subject of atoms and molecules may be read up to advantage in Cooke's "New Chemistry," Wurtz's "Atomic Theory," Cooke's "Chemical Philosophy," or Remsen's "Theoretical Chemistry."

CHAPTER III.

HYDROGEN.

In the preceding chapters reference has been made to the fact that water is composed of hydrogen and oxygen. We may now study hydrogen, oxygen, and water separately and in detail.

Hydrogen, although it had been obtained and partly examined by several earlier investigators, was first accurately studied by Cavendish in 1766. In 1781 he made the additional discovery that water is the only product of its combustion; and, on account of this fact, Lavoisier gave it its present name, which signifies "water-producer." It may be easily obtained from water as follows:

Experiment 5.—Wrap a bit of sodium as large as a pea in some wire-gauze, and hold it by a handle of stout wire under the mouth of an inverted test-tube filled with water in a pneumatic trough. Instead of the latter piece of apparatus, a common, deep earthenware dish full of water may be used. The test-tube should be filled with water *completely;* then, by closing its mouth with the thumb, it may be inverted and placed easily in position. The sodium will at once be attacked by the water, bubbles of gas will be evolved and rise into the tube, and soon the latter will be full. Again close the mouth of the tube with the thumb, and bring it mouth uppermost. Now, upon removing the thumb, and instantly applying a match, the gas in the tube will

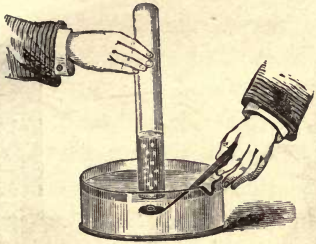

FIG. 2.—Preparation of Hydrogen with Sodium.

ignite, and burn with a pale, bluish flame. The gas is *hydrogen.* Since the bit of sodium may produce a slight explosion, it is prudent in this experiment to wear stout gloves.

In the foregoing experiment the sodium withdraws oxygen from the water, setting hydrogen free. When steam is passed through a gun-barrel or piece of gas-pipe filled with iron-filings and heated to redness, a similar change takes place; the oxygen of the steam being retained by the iron, so that only hydrogen escapes at the farther end of the apparatus. But, for preparing hydrogen in quantity, the subjoined method is the most convenient:

EXPERIMENT 6.—Place a quantity of granulated zinc (prepared by pouring melted zinc from a height of three or four feet into cold water) in a gas delivery-flask (Fig. 3), and cover it with dilute hydrochloric acid. Iron-filings may be used instead of zinc, and sulphuric acid in place of hydrochloric.*

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* Some druggists and dealers in chemicals still retain for this acid the nearly obsolete name of muriatic acid.

In either case hydrogen will be copiously evolved; and it may be collected over water in a number of small, wide-mouthed bottles. The first portions of gas should be allowed to escape, since they will be contaminated with the air which originally filled the apparatus. By applying a flame to the mouth of one of the little bottles, the inflammability of hydrogen may again be recognized.

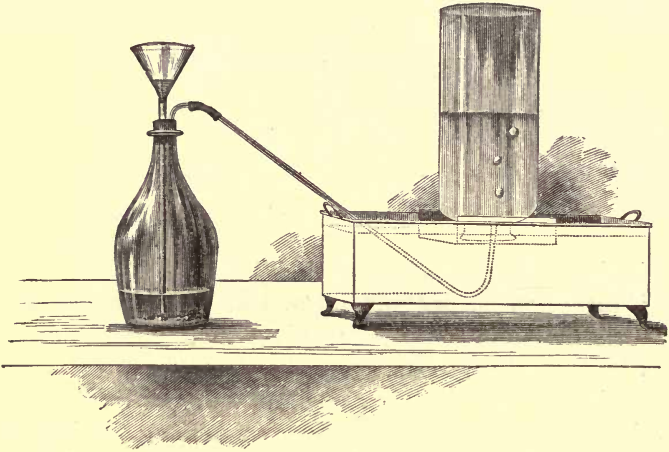

FIG. 3.—Preparation of Hydrogen.

Hydrogen, when perfectly pure, is a colorless, tasteless, odorless gas. As ordinarily prepared, however, it is apt to be disagreeably scented by impurities derived from the materials used in its manufacture. It is found in Nature, in the free state, among the gases exhaled by certain volcanoes; and it is also contained in many meteoric irons. Not only iron, but several other metals also, notably palladium, have the property of absorbing (or *occluding*) considerable quantities of hydrogen. Since metals containing occluded hydrogen exhibit in some degree the properties of alloys, it has been suggested that hydrogen ought to be classed as a metal also; and some chemical reasons, which will be cited further on, tend to support this view. Hydrogen exists in enormous quantities in the atmosphere of the sun, and in most of the other self-luminous heavenly bodies, its presence there being revealed to us by the spectroscope. It is an important constituent of coal-gas; and in the combined state we find it not only in water, but in nearly all animal and vegetable substances, in petroleum, and in a great many artificial products.

We have already seen that hydrogen is inflammable, and that its flame is but feebly luminous. It is, however, exceedingly hot, as the following experiment will show:

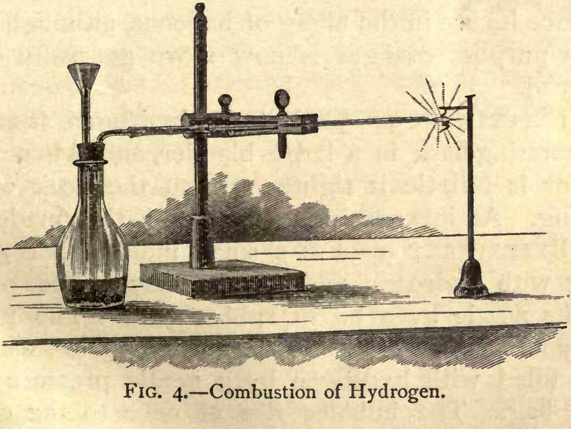

FIG. 4.—Combustion of Hydrogen.

EXPERIMENT 7.—Generate hydrogen as in Experiment 6; only, instead of collecting it over water, allow it to issue into the air through a long glass tube drawn out to a fine jet at the end. Allow the gas to escape for some time, until all the air originally contained in the flask has been expelled; then light the jet of gas and observe the character of the flame. Now insert in the flame a little fine coil of platinum wire. It will at once become brilliantly white-hot. If the gas is kindled while air remains in the flask, a violent explosion will ensue. By holding a cold test-tube inverted over the hydrogen-flame, the formation of drops of water as a product of combustion may be observed.

Hydrogen is incapable of supporting respiration; hence, small animals immersed in it soon die. The pure gas may, however, be inhaled to a limited extent without danger. When the lungs are filled with it, even the gruffest voice becomes curiously shrill and hollow.

Hydrogen is the lightest of all known substances. Hence its use in the filling of balloons, although for this purpose coal-gas is now more generally employed.

EXPERIMENT 8.—Collect the hydrogen from a generating-flask in a large bladder, and, when the latter is full, tie it tightly around the neck with string. An inexpensive toy-balloon is thus made.

EXPERIMENT 9.—Fill a small india-rubber gas-bag with hydrogen, and attach a clay tobacco-pipe to its nozzle by a bit of rubber tube. The pipe may now be used for blowing soap-bubbles, which are filled with hydrogen by a gentle pressure on the bag. The bubbles rise at once to the ceiling, on account of their remarkable lightness. By touching each bubble with a candle-flame, the inflammability of hydrogen may be further illustrated.

EXPERIMENT 10.—Hydrogen may be poured from one bottle into another, but it must be poured *upward*. One of the small bottles filled in Experiment 6 will do for this experiment. When the gas has been transferred, it may be recognized in the second bottle by its inflammability. (See Fig. 5.)

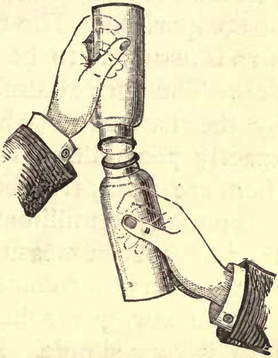

FIG. 5.—Pouring Hydrogen up.

The weight of one litre (or cubic decimetre) of hydrogen, measured at the temperature of 0° centigrade, and under a barometric pressure of 760 millimetres, is only 0.0896 gramme.* This weight is called a *crith*, and is an important unit of weight in all gas calculations. In the subjoined table it is compared with the weight of equal bulks of air, water, and platinum—the latter being the heaviest substance known.

One cubic	decimetre of	hydrogen	weighs	0.0896	gramme.
"	"	air	"	1.2932	"
"	"	water	"	1000.0000	grammes.
"	"	platinum	"	21500.0000	"

Hence, air is 14.43 times, water a little over 11,000 times, and platinum about 240,000 times heavier than hydrogen.

In many chemical calculations the volume occu-

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* Tables of metric weights and measures, and of the different thermometric scales, may be found in the Appendix.

pied by a given quantity of gas is a very important factor. Since the volume of a gas depends upon conditions of temperature and pressure, we must take these agencies into account, and, for convenience, we must first establish some definite standards of comparison. The normal, or standard, temperature is assumed to be 0° centigrade, or 32° Fahrenheit. The normal atmospheric pressure is indicated by the barometer when the mercurial column is exactly 760 millimetres high. Volumes of gases, then, are always to be compared at 0° centigrade, and under 760 millimetres pressure; and, whenever they have been measured under other conditions, it is customary to reduce them to these standards.

The law governing the expansion of gases by heat is very simple. For present purposes it may be stated thus: *All gases expand equally for equal rises of temperature.* Although this is only approximately true, its variations from absolute accuracy need not be considered in ordinary calculations. The errors introduced are so small that they may be safely ignored; just as in measuring the width of a room a thousandth of an inch more or less counts for nothing. For each degree centigrade, a gas, measured originally at 0°, will expand $\frac{1}{273}$ of its bulk; thus:

273 volumes of air at 0° become—

274	"	at	1°,
275	"	"	2°,
276	"	"	3°,
$273+t$	"	"	t°,
272	"	"	-1°,
271	"	"	-2°, etc.

If this rule were absolutely true, then, at 273° below zero, the volume of a gas would become nothing, and matter would absolutely vanish. Accordingly, 273° below the centigrade zero is called the *absolute zero of temperature.* Of course, this value has no experimental meaning, since it can never be reached: but it has some mathematical importance. Gases cease to be gases, and condense to liquids or solids, long before reaching so low a temperature.

Suppose, now, we have two volumes (two litres, or two cubic feet, or whatever units you please) of hydrogen at 0°, and wish to calculate what its bulk would be if heated up to 25°. The formula is as follows:

$$273 : 273 + 25 :: 2 : x.$$

Conversely, if we measure two volumes at 25°, and wish to reduce it to 0°:

$$273 + 25 : 273 :: 2 : x.$$

Again, let us take twelve volumes of gas at 37°, and wish to determine its volume after cooling to 23°:

$$273 + 37 : 273 + 23 :: 12 : x.$$

In some cases we have to deal with volumes of gases below 0°. Then, instead of adding, we subtract the given number of degrees from the standard volume, 273. In short, we always express the volume of a gas at 0° by 273, assume an increase or decrease, as the case may be, for each degree of difference from 0°, and then, by a simple proportion, the reduction to 0° may be easily made.*

The changes in the volume of a gas due to va-

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* Most of the problems which arise in chemical calculations are most clearly and logically stated in the form of simple proportions. Every pupil should, therefore, become accustomed to this method of computing.

riations in pressure are governed by a very simple law, as follows: *The volume of a gas is inversely proportional to the pressure.* This is termed the law of Boyle and Marriotte, having been independently discovered by these two investigators. If we double the pressure under which a gas is kept, we halve its volume; if we halve the pressure, we double the volume, and so on. This relation is conveniently expressed by the formula $P_1 : P :: V : V_1$; in which V represents the volume under the pressure P, and V_1 the volume under the altered pressure P_1. For example, suppose we have measured ten volumes of hydrogen when the barometer stood at 771 millimetres, and we wish to calculate what it would become at 760 millimetres:

$$760 : 771 :: 10 : x.$$

Here we see that, under the lower pressure, the gas has expanded slightly. Conversely, if ten volumes have been measured at 760 millimetres, they will become less than ten at 771 millimetres, thus:

$$771 : 760 :: 10 : x.$$

The law governing pressures is, like that relating to temperatures, only a very close approximation to the truth. Its variations from accuracy can, however, only be detected by the most refined experiments.*

By intense cold and great pressure all gases are condensible to liquids, and even into the solid state. For hydrogen, this was first experimentally accom-

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* The experimental evidence for these laws may be read up in a volume upon physics. A good theoretical discussion of them may be found in the third chapter of Cooke's "Chemical Philosophy," new edition.

plished by MM. Cailletet and Pictet (working independently of each other) at the close of the year 1877. By Pictet it was cooled to −140° centigrade under a pressure of 650 atmospheres. (The pressure exerted by the air in maintaining a barometric column of mercury at the height of 760 millimetres is called one atmosphere.) Under these conditions hydrogen became visible as a steel-blue liquid, a portion of which solidified as it issued from the apparatus, and fell to the ground in grains. These emitted a shrill, metallic sound as they struck the floor, thus emphasizing the idea that hydrogen is really a metal. Many metals can be converted into gases at high temperatures; mercury becomes gaseous at 350° centigrade, and is liquid under ordinary circumstances. The gaseous nature of hydrogen, therefore, has nothing to do with the question whether it is metallic or non-metallic. The *chemical* significance of these terms will appear in later chapters.

CHAPTER IV.

OXYGEN.

Oxygen, which was discovered by Priestley in 1774, and a little later, but independently, by Scheele, is the most abundant of all the elements. Uncombined, but mixed with nitrogen, it constitutes one fifth of the atmosphere; combined, it forms eight ninths of the material composing water, and about one half the weight of all the rocks. It is also a very important constituent of animal and vegetable matter.

Oxygen was originally prepared by heating mercuric oxide (see Experiment 2), mercury being left behind, while the oxygen was given off. This method, however, is inconvenient, and is now replaced in ordinary practice by the following cheaper process:

Experiment 11.—Take a stout test-tube, or, better, a piece of glass combustion-tubing sealed at one end, and close its mouth with a perforated cork, through which is inserted a delivery-tube, also of glass. Mix thoroughly upon a sheet of paper equal weights of potassium chlorate and manganese dioxide, taking care that both are perfectly pure and dry. Fill the test-tube one third full with this mixture, and heat carefully over a spirit-lamp or a

Bunsen gas-burner. Oxygen will be given off copiously, and may be collected either in a rubber gas-bag, or in several bottles over water in the pneumatic trough. (Fig. 6.) When oxygen is to be prepared in large quantities, a copper or iron retort is used instead of a glass tube. For safety, several precautions ought to be observed. First, it is well to heat the manganese dioxide to redness in an iron dish before using it, in order to burn out any deleterious impurities. Were particles of organic matter or charcoal to be present, a dangerous explosion might ensue. Secondly, the upper portions of the mixture in the tube should be heated first, and later the lower portions. Thirdly, the heat should be so regulated that the oxygen will be given off in a steady, tranquil stream ; not in sudden gusts, explosively.

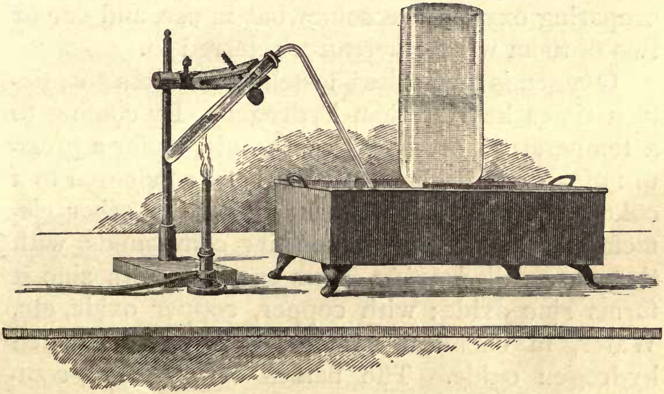

FIG. 6.—Preparation of Oxygen.

In this experiment the potassium chlorate, which consists of potassium, chlorine, and oxygen chemically combined, is decomposed; the oxygen being set free, while potassium chloride, a compound of potassium and chlorine, remains behind. The manganese dioxide undergoes no change, but in some way it facilitates the decomposition of the chlorate. This kind of action, in which a body assists a chemical process without being itself altered, is often met with, and is termed *catalytic* action. Some cases of *catalysis* are easily explained, but this particular case awaits an explanation. Several other processes for preparing oxygen are somewhat in use, and one or two of them will be hereafter referred to.

Oxygen is a colorless, tasteless, odorless gas, sixteen times heavier than hydrogen. By cooling to a temperature of $-140°$ centigrade, under a pressure of 320 atmospheres, it has been condensed to a colorless liquid. It unites with all the other elements, except fluorine, and its compounds with them are called *oxides*. For example, with zinc it forms zinc oxide; with copper, copper oxide, etc. Water, in chemical nomenclature, can be called hydrogen oxide. The names of chemical compounds are intended to express, more or less perfectly, their composition. When oxygen unites with other substances, the process is termed *oxidation*.

The most characteristic property of oxygen is its power of sustaining combustion. In nearly all cases combustion is merely oxidation accompanied by the development of heat and light. When oxygen is excluded from a burning body, the fire goes out. In the air, we have one fifth of oxygen diluted with four fifths of nitrogen, the latter element being inert and exerting no direct influence upon combustion whatever. Naturally, combustion takes place much more vividly in pure oxygen than in diluted oxygen (or air), as the following easy experiments will show:

EXPERIMENT 12.—Blow out a lighted candle, leaving a glowing spark at the end of the wick. Lower the candle into a bottle or jar of oxygen, and the wick will relight, burning far more brightly than before.

EXPERIMENT 13.—Charcoal burns in the air without flame, with only a dull-red glow. Plunge a bit of ignited charcoal into a jar of oxygen, and it will burn brilliantly.

EXPERIMENT 14.—Kindle a bit of sulphur in a deflagrating spoon, and note the insignificant flame. Now lower it into pure oxygen, and the combustion will become exceedingly vivid (Fig. 7).

EXPERIMENT 15.—Repeat the last experiment, using a much larger jar of oxygen, and burning phosphorus instead of sulphur. The combustion will be so dazzlingly brilliant that the experiment has sometimes been fancifully called "the phosphoric sun."

FIG. 7.—Combustion in Oxygen.

EXPERIMENT 16.—Some substances which do not ordinarily burn in air burn easily in pure oxygen. For example, fasten a bit of steel watch-spring to a stout wire, and dip the end of it in melted sulphur. Kindle the latter and immerse the spring in oxygen. Presently the steel itself will ignite, burning brilliantly and sending forth a shower of sparks. It will be well to cover the bottom of the oxygen-jar with sand, to catch any particles of melted metal which may fall.

Oxygen is also essential to respiration. Exclude it from the lungs, and death follows, as in cases of drowning, when the lungs become filled with water. Inclose a small animal in a limited volume of air, and it lives only until the supply of oxygen contained in it is exhausted. In pure oxygen it will live much longer, but the vital processes will go on too violently and rapidly, and death will result.* Even the fishes need oxygen, and they secure it through their gills from the air which is dissolved in the water. In a shallow pool insufficiently supplied with air a fish will soon die.

Oxygen is administered by physicians to a certain extent as a remedy in cases of impeded breathing. A croupy or asthmatic patient, for instance, can not get enough air for proper respiration; but upon breathing a little pure oxygen he will experience great relief. When the lungs are filled with oxygen instead of air, it is possible to "hold the breath" much longer than ordinarily—a fact which might be used by divers. Oxygen is now made for sale in most of our large cities. It is used chiefly in the calcium-light (see next chapter), and is stored up under compression in strong iron cylinders.

The fact that oxygen dissolves somewhat in water, as hinted in a preceding paragraph, is one of vast importance in the economy of Nature. In the

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* In the chapter upon carbon the phenomena of combustion and respiration will be treated more fully.

falling of the rain, the agitation of the waves, and the flowing of streams, water is being constantly charged with fresh supplies of air. The oxygen thus absorbed at once attacks the decaying animal and vegetable matter which is continually flowing into rivers, lakes, and oceans, and by a process of slow combustion literally burns it up. Thus oxygen becomes a great disinfectant, transforming noxious substances into simpler and harmless compounds, and keeping the waters of our planet always sweet and clean. In a similar way it oxidizes injurious vapors in the air, and is effective in the removal of all kinds of corruption from the face of the earth. All decay involves the phenomenon of oxidation.

Many elements, and possibly all of them, are capable of existing in more than one modification. For example, carbon exists as charcoal, as graphite or " black-lead," and as diamond ; and similar properties are strikingly displayed by phosphorus and sulphur. This phenomenon is called *allotropy*, and charcoal, graphite, and diamond are termed *allotropic* modifications of carbon.

When an electrical machine is rapidly worked, or when a series of electrical sparks are passed through air, a peculiar odor, something like that of burning sulphur, soon becomes noticeable. This odor is due to the formation of an allotropic modification of oxygen, to which the name of *ozone* has been given.

EXPERIMENT 17. — Suspend a freshly-scraped stick of phosphorus in a jar containing a little water, so that it shall be partly immersed. It will slowly oxidize ; and soon the air in the jar will acquire the peculiar odor of ozone.

Ozone has properties quite unlike those of ordinary oxygen. It not only has a characteristic suffocating odor, but it exhibits a remarkable chemical activity, attacking and tarnishing metals like silver and mercury, which common oxygen does not affect at all. It bleaches many vegetable colors, like indigo, deodorizes putrefying animal matter, and corrodes such substances as cork, India-rubber, etc. A common test for it is paper soaked in a solution of potassium iodide and starch. Moist slips of such paper, exposed to the action of ozone, turn blue; because the ozone liberates iodine from the potassium iodide, and iodine forms a blue compound with starch.

In ordinary experiments only a very small portion of any mass of oxygen can be transformed into ozone. The transformation is, however, attended by a shrinkage in the volume of the oxygen, so that ozone is really oxygen in a more concentrated state. Three volumes of oxygen would yield, if wholly converted into ozone, only two volumes of the latter; whence it is easy to see that, bulk for bulk, ozone is half as heavy again as oxygen. The full significance of this fact will appear in a later chapter. Quite recently, ozone has been liquefied by the application of cold and pressure. Liquid ozone has a deep indigo-blue color, and is less volatile than liquefied oxygen.

Ozone is continually being produced in nature, both by the electric discharges which take place during thunder-storms, and by the many phenomena of slow oxidation which may be observed in the vegetable kingdom. It undoubtedly plays an important part in the world as a natural disinfectant, but upon this point much remains to be discovered. At one time a third variety of oxygen, named antozone, was supposed to exist; but the evidence in favor of it is now generally considered unsatisfactory.

CHAPTER V.

WATER.

ALTHOUGH oxygen and hydrogen gases may be mixed together in any proportions, they unite chemically to form only two real compounds, both of which at ordinary temperatures are liquids. One contains exactly twice as much oxygen as the other, and on this account the names hydrogen monoxide and hydrogen dioxide are respectively applied to them. In chemical nomenclature numeral prefixes have to be frequently employed.

When oxygen and hydrogen combine directly, that is, without the intervention of other substances, only hydrogen monoxide or water is produced. The dioxide is prepared by indirect, roundabout processes.

The formation of water from oxygen and hydrogen may be brought about either by the passage of an electric spark through the mixed gases, or by the agency of heat. Whenever hydrogen or any compound of hydrogen is burned, water is produced; as was partly demonstrated in Experiment 7. All ordinary illuminating materials, such as coal-gas, oils, candles, etc., contain hydrogen; and if a piece of cold porcelain be held for a moment over their flames, the deposition of dew will show that water is actually formed.

Under ordinary circumstances the combustion of hydrogen takes place quietly; but if it be burned in pure oxygen some extraordinary phenomena may be observed.

EXPERIMENT 18.—Fill an India-rubber gas-bag with a mixture of two parts by volume of hydrogen and one part of oxygen. Then, as in Experiment 9, attach a clay pipe to the bag and use the gaseous mixture for blowing soap-bubbles. Each bubble, when touched with a lighted candle, will explode with a violent report. If a heap of bubbles be blown in a common tin basin and ignited, the explosion will be deafening. Before applying a flame to any of the bubbles the stop-cock of the bag should be closed and the bag itself removed. Serious accidents have happened from the ignition of large mixtures of oxygen and hydrogen. Even coal-gas and common air will give a powerfully explosive mixture, fully as dangerous as gunpowder. This is shown by the terrible explosions which sometimes occur when a light is carelessly carried into a room in which gas has been escaping.

This experiment shows us that the formation of water from its elements is attended by a remarkable development of force or energy. This force may be best measured in the form of heat: and it is found that more heat is produced in this chemical change than in any other chemical change whatever. The usual unit of heat is the quantity of heat needed to raise the temperature of one gramme of water from 0° to 1° C.; and in the combustion of one gramme of hydrogen 34,462 such units of heat are set free. A gramme of charcoal, burning, yields only 8,080 heat-units—a figure in striking contrast with the foregoing. When hydrogen burns in ordinary air, just as much heat is developed as if the combustion took place in pure oxygen; but the temperature of the flame is lower—partly because the heat is generated more slowly, and partly because much of it is expended in warming the nitrogen with which the oxygen of the atmosphere is diluted. By using pure oxygen instead of air, an enormously high temperature may be attained and utilized.

Although mixtures of oxygen and hydrogen explode violently when ignited, the two gases may be made to burn together quietly by mingling them just at the moment of combustion. This is done in the compound (or oxyhydrogen) blow-pipe invented by Dr. Hare. In this apparatus (Fig. 8) the oxygen and hydrogen are contained in two separate bags or cylinders. They are mixed just at the tip of the burner (Fig. 9), which consists of two tubes, one within the other. Through the central or inner tube oxygen is allowed to flow, while the outer tube connects with the hydrogen-reservoir. The hydrogen is first turned on and kindled, then the oxygen

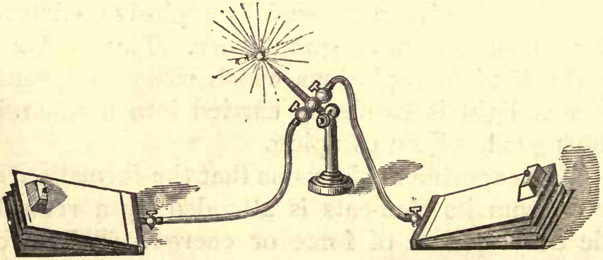

Fig. 8.—Oxyhydrogen Blow-pipe.

is admitted; the flow of both gases being carefully regulated by stop-cocks, and by pressure on the bags. The flame, although almost non-luminous, is intensely hot; and many substances which were

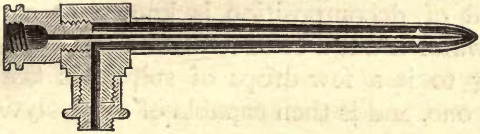

FIG. 9.—Oxyhydrogen Blow-pipe Tip.

once deemed infusible melt in it easily. Platinum, for example, melts like wax before the compound blow-pipe, although in the hottest furnace it only softens. In the metallurgy of platinum this fact is carefully utilized. Some metals, like silver, are vaporized by the heat of the oxyhydrogen jet, while others burn in it brilliantly. A steel file, for instance, is easily consumed, sending forth a magficent shower of sparks as it burns.

When any substance capable of resisting the excessively high temperature is inserted in the oxyhydrogen flame, it becomes intensely luminous. This fact is applied in the calcium or Drummond light, now extensively used in stereopticon exhibitions and for theatrical effects. This light consists simply of a small cylinder of common lime, upon which the flame of a compound blow-pipe is allowed to play. It rivals the electric light in intensity.

Up to this point we have been considering only the *qualitative* composition of water, and the phenomena attending its formation. We now need to enter upon *quantitative* discussions, both as to the volumes and the weights of the oxygen and hydrogen which unite.

Whenever a current of electricity is passed through a liquid capable of conducting it, that liquid, if compound, will be decomposed. This method of decomposition is known as *electrolysis*. Pure water is not a conductor of electricity, but by adding to it a few drops of sulphuric acid it becomes one, and is then capable of electrolytic analysis.

EXPERIMENT 19.—Fill and invert two test-tubes in a vessel of water slightly acidulated with sulphuric acid. Now bring under their mouths the two terminal wires of a small galvanic battery, best of a couple of Grove, Bunsen, or Daniell cells (Fig. 10).

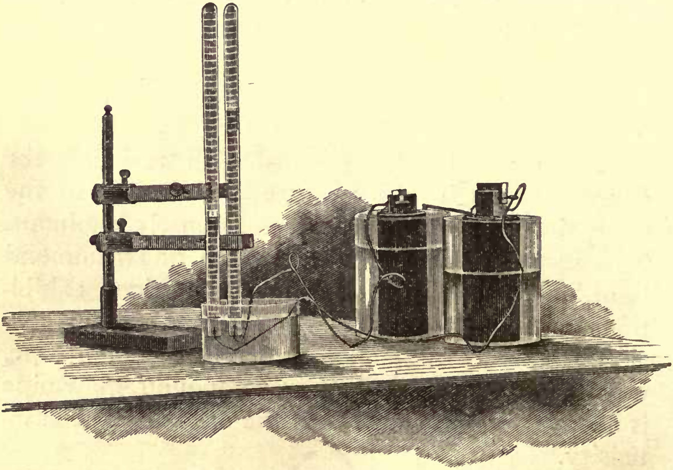

FIG. 10.—Electrolysis of Water.

Bubbles of gas will slowly form (more rapidly with a more powerful battery) and rise into the test-tubes, displacing the water which they at first contained. Allow this action to continue until enough gas has accumulated for convenient examination, and notice that one tube contains just twice as much as the other. By applying a match to the more voluminous gas it may be identified as hydrogen ; while by plunging an ignited splinter of wood into the contents of the other tube oxygen may at once be recognized. By analysis, therefore, water yields two volumes of hydrogen to one of oxygen. In this experiment the battery-wires, as far as they dip into the acidulated liquid, should terminate in slips of platinum.

The foregoing method of analysis is not rigidly exact, for the reason that traces of the gases evolved, and rather more of the oxygen than of the hydrogen, remain dissolved in the water. Synthetic methods, though more difficult, are better.

When an electric spark, either from an electrical machine, a Leyden-jar, or an induction-coil, is passed through a mixture of hydrogen and oxygen, the two gases unite with an explosion. For quantitative purposes this experiment is usually performed in a graduated glass tube, called a eudiometer, and the spark is transmitted between two platinum wires which are melted into the glass at the closed upper end (Fig. 11). In such a tube the gases can be accurately measured ; and it is found that when just two volumes of hydrogen and one of oxygen are taken, the union is complete. If the mixture of gases contains more than two thirds hydrogen or more than one third oxygen, the excess of either element simply serves to dilute the rest, and remains unaltered after the explosion. The oxygen and hydrogen under these circumstances *combine only* in the proportions above indicated.*

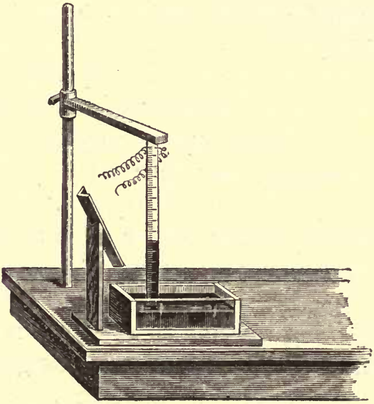

FIG. 11.—Eudiometer.

In experiments upon the union of gases by volume an important question always arises—namely, Is the volume of the product the same as that of the original mixture, or does condensation occur? Suppose, for example, that two litres of hydrogen combine with one litre of oxygen, and that we measure the volume of the resulting water in the form of steam. We shall find that, if we compare the steam with the component gases at identical temperatures and under the same pressure, only two litres of steam have been formed. In other words, the three original volumes of elementary gases have condensed to two volumes during union. When we

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* For class-room illustration this experiment may be roughly performed with improvised apparatus, as far as demonstrating the effect of an electric spark is concerned. *Accurate* work is hardly possible under such circumstances.

come to consider this fact in its relations to other facts further on, we shall see that it has a very important bearing upon the theories of chemistry. For the present we may use it to determine the weight of steam as compared with that of hydrogen. One volume of oxygen weighs sixteen times as much as an equal volume of hydrogen. Hence the three volumes of elementary gases which unite to form water must weigh $1 + 1 + 16 = 18$ times as much as one volume of hydrogen. But this is also the weight of two volumes of steam, so that one volume of steam must weigh half as much, and be nine times heavier than hydrogen. Furthermore, these figures give us the composition of water by weight. The one volume of oxygen must be just eight times as heavy as the two volumes of hydrogen, and accordingly water consists of one part by weight of the latter element to eight parts of the former. This ratio of one to eight is more commonly written two to sixteen, for reasons which will appear in a later chapter.

The different phenomena and substances with which chemistry has to deal are so intimately connected one with another, that it is always desirable to verify important facts by several distinct lines of investigation. Since the composition of water is a matter of very great importance, we can not rest content with the *volumetric* analysis and synthesis given above, much as they confirm each other, but we must make use of other modes of demonstration also. For the composition of water by weight we have so far only an indirect estimation; and for additional proof an actual synthesis by weight must be resorted to. This is best accomplished with the aid of copper oxide, a substance containing a definite quantity of oxygen in a condition very available for our purposes.

EXPERIMENT 20.—Place a quantity of dry copper oxide in a tube of hard glass, and connect the latter, held horizontally, with the exit-tube of a flask in which hydrogen is being generated. When the apparatus is full of hydrogen, so that an explosion due to admixed air may be no longer feared, heat the copper oxide carefully to near redness (Fig. 12). As the hydrogen streams over it, oxygen will be withdrawn and water will be formed; which, as steam, will issue from the farther end of the tube. When the operation is complete, all of the black oxide will have been reduced to pure, bright, metallic copper.

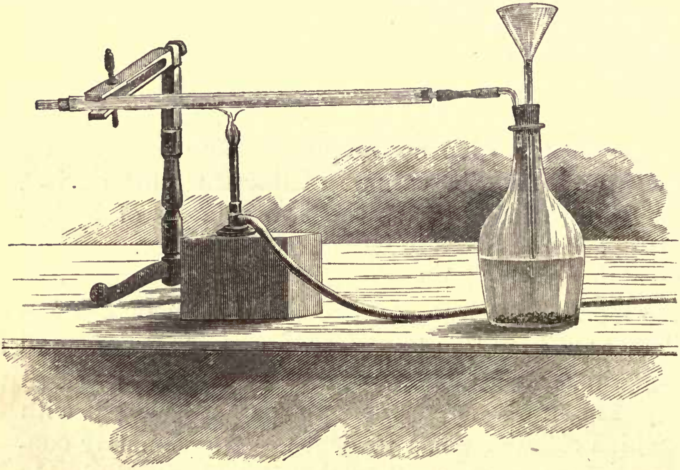

FIG. 12.—Synthesis of Water.

This experiment, with some delicate refinements, gives us the means for accurately ascertaining the weight-composition of water. We have only to weigh the copper oxide before the experiment, and afterward to weigh the remaining metallic copper and the water which has been formed, and all the necessary data are at our disposal. The difference between the weights of the copper oxide and the copper is plainly the weight of the oxygen in the water produced. This weight, subtracted from that of the water, gives us, of course, the weight of the hydrogen. By this method, water is found to contain, by weight—

88.89 per cent of oxygen,
11.11 " " hydrogen,
100.00 total.

These figures give us, in strict accordance with those calculated from the volumes of the two gases, the ratio of one to eight, or two to sixteen,* between the weights of oxygen and hydrogen in water. Water, then, contains, by volume, two of hydrogen to one of oxygen, these three volumes being condensed by union into two. By weight it contains two parts of hydrogen and sixteen of oxygen—figures which we shall have occasion to use repeatedly hereafter.

Water, or hydrogen monoxide, is a transparent, tasteless, odorless liquid. In small quantities it appears colorless also, but in thick layers it is found to have a decided blue tint. Its physical properties are of the highest importance, inasmuch as they

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* The ratio actually deduced from all the best experiments is 2 : 15.9633. The latter figure is so nearly 16 that 16 may fairly be used in ordinary calculations.

furnish some of the most convenient standards with which to compare those of other substances. Our thermometric scales, for example, depend upon the boiling of water and the melting of ice; the boiling-point being taken as one standard of temperature and the melting-point as another. In the centigrade scale, which alone is used in this book, the temperature at which ice melts or water freezes is arbitrarily put at zero, while the boiling-point is given the value of 100°. The interval between is divided into one hundred equal parts, and similar degrees are marked off for temperatures above or below the two standards. The Fahrenheit scale, which is the one in common use, assumes 32° for the freezing-point of water and 212° for the boiling-point, dividing the space between into one hundred and eighty degrees.

When boiled, water yields a larger volume of vapor than any other known liquid. One litre of water, measured at 0° C., converted into steam at 100°, will give 1,696 litres of the latter. Hence the common expression that "a cubic inch of water yields a cubic foot of steam" is approximately true. But few other liquids out of the hundreds known give even one third as great a volume of vapor.

Upon cooling, water again behaves remarkably. It contracts regularly until the temperature of 4° is reached, at which degree it attains its *maximum density*. Cooled still further, it expands, and at 0° it solidifies into ice, undergoing another more sudden expansion. It is this expansive force which breaks bottles and pitchers in which water is allowed to freeze, and which gives to frost its great power in disintegrating rocks. Because of the expansion, ice is lighter than water and floats upon it; were it to sink, fresh surfaces of liquid would be exposed to freezing during winter, until our lakes and rivers were frozen solid. Such masses of ice could not be melted by the summer's heat, fish-life would become impossible, and the temperate zones would in time be almost frigid. When the vapor of water is suddenly chilled, snow is formed, and every flake exhibits a regular crystalline structure. Each snow-crystal is a symmetrical, six-pointed star, one varying from another only in minor particulars (Fig. 13). Form is as distinct a property of substances as color, taste, or smell; and every solid has its own characteristic shape, in which, if left to themselves, its molecules become arranged in accordance with rigid mathematical laws.

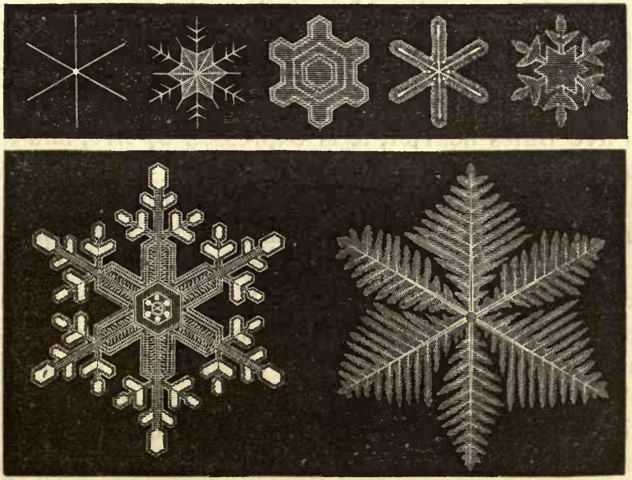

FIG. 13.—Snowflake Crystals.

As regards weight, water is again an important standard. In the metric system the unit of weight is the gramme; and this is defined as the weight of a cubic centimetre of water measured at its temperature of maximum density. A cubic decimetre of water, or a litre, weighs just a thousand grammes, or one kilogramme. The most exact weights and measures, therefore, depend for their accuracy upon a precise knowledge of some of the properties of water.

In dealing with solids and liquids, specific gravity or density is always referred to water as the unit of comparison. If a body is twice as heavy as water, bulk for bulk, its specific gravity is said to be two; if five times heavier, it is expressed by five, and so on. The specific gravity of a gas or vapor is now generally referred to hydrogen as unity, although in some works air is still retained as the standard.*

As a solvent, water far exceeds every other liquid known. Certain liquids, like alcohol or chloroform, will dissolve some substances which water can not attack, but in the long run water leads them all. As a general rule, with comparatively few exceptions, solids dissolve more easily in hot water than in cold. Gases, on the other hand, are more soluble in cold water. Some substances, like sugar, dissolve easily and in large quantity in water; others, as for example gypsum, dissolve but sparingly; but for each one there is a limit beyond which solubility can not go. These facts may advantageously

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* Some of this material belongs more properly in a work on physics, so that fuller discussion is impracticable here. Such physical data as have chemical importance will be introduced here and there throughout this volume.

be verified by the student with self-devised experiments upon salt, sugar, alum, and such other soluble bodies as may happen to be most readily available. The phenomenon of solution is one which has not yet been fully explained; it is *probably* due to a very weak kind of chemical attraction between the solvent liquid and the substance dissolved.

Because of its great solvent properties, natural water is never strictly pure. Rain-water contains gaseous impurities, and even traces of solid matter dissolved in it; while river, spring, well, and lake waters absorb a variety of substances from the soil. Evaporate any ordinary drinking-water to dryness on a slip of clean, bright platinum-foil, and you will obtain visible traces of a solid residue. In sea-water, salt lakes, and mineral springs, saline substances are present in large quantities. Effervescent waters, like those of the Saratoga springs, are also heavily charged with a well-known gas, carbon dioxide or carbonic acid. Waters nearly free from solid ingredients are called *soft* waters. Waters containing much lime in solution are called *hard*. Perfectly pure water is so tasteless as to seem flat and undrinkable. Only after it has been *aërated* by exposure to the air does it become palatable.

Water may be readily freed from suspended sediments either by settling in large tanks or by filtration. On the large scale it is best filtered by allowing it to percolate through layers of charcoal and sand, but in the laboratory filters of paper are commonly used. A circular sheet of unsized paper is doubled, and then folded again at right angles to the crease first made. By lifting one of the folds away from the other three, a hollow cone of paper is obtained which will fit snugly to the sides of a glass funnel. When water containing sediment is poured through this arrangement, the suspended solids are retained by the paper, and the liquid is transmitted clear (Fig. 14).

In order to obtain water free from dissolved impurities, resort must be had to distillation. This process consists simply in boiling the water away, and then condensing and collecting it from the steam. Distillatory apparatus may be made after a great variety of patterns, according to the exact use

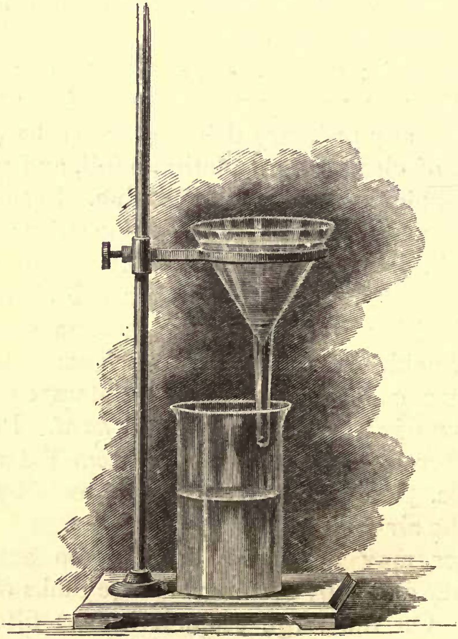

FIG. 14.—Filtration.

to which it is to be applied. For school purposes, a glass retort will suffice, arranged as shown in Fig.

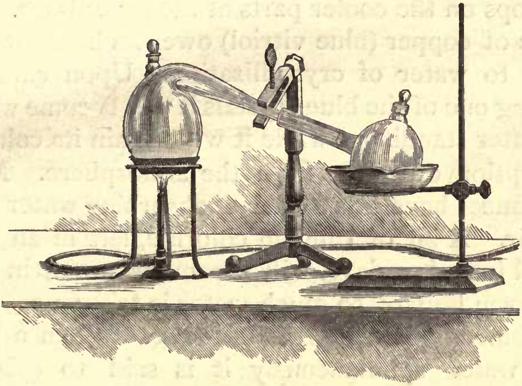

FIG. 15.—Distillation.

15. The retort, mounted on a convenient stand, is half filled with water and heated by a lamp placed below. To diminish the danger of breaking, the bottom of the retort should be separated from the direct flame by a sheet of fine wire-gauze. The neck of the retort dips into a flask called a receiver, which, together with the neck, is kept cold by the application of wet cloths. When the water in the retort is boiled, the steam passes over to be condensed in the receiver.* From gaseous impurities water may be freed by simple boiling.

Water is capable of entering into chemical union with many other substances. A great number of crystalline salts contain definite quantities of it, in a

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* The author purposely describes the apparatus in its very simplest form. Schools having more elaborate appliances will of course use them.

condition known as *water of crystallization.* Heat a crystal of alum in a glass tube, and it will give off water, which may be recognized by its condensing in drops on the cooler parts of the tube above. Sulphate of copper (blue vitriol) owes its brilliant blue color to water of crystallization. Upon carefully heating one of the blue crystals it will become white; and after standing a while it will regain its color by absorption of water from the atmosphere. Many substances have this power of absorbing water from the air. A bit of calcium chloride, left in an open vessel for a few days, will become wet, and in time will even liquefy, so much water is taken up. This phenomenon is called *deliquescence.* When a body *loses* water spontaneously it is said to *effloresce.* Many minerals contain water of crystallization, and water is an essential and important constituent of all animals and vegetables.

The second compound of hydrogen and oxygen, hydrogen dioxide,* is a very interesting substance, but hardly important enough for extended description here. It is a liquid nearly half as heavy again as water, and it actively bleaches vegetable colors. As a powerful oxidizer it behaves very much like ozone.

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* Sometimes called peroxide of hydrogen.

CHAPTER VI.

NITROGEN AND THE ATMOSPHERE.

NITROGEN, which was discovered by Rutherford in 1772, occurs abundantly in the atmosphere, and also as an important constituent of animal and vegetable matter. It is furthermore contained in very many artificial substances; as, for example, nitric acid, ammonia, saltpeter, nitroglycerine, and so on. In the air it is found to be mixed with oxygen; and it is most readily isolated by simply withdrawing the latter element from it.

EXPERIMENT 21.—Place a bit of carefully dried phosphorus, as big as a pea, upon a piece of flat cork, and float it in a large earthen dish half full of water. Kindle the phosphorus, and then cover it with a capacious glass jar or bell-glass, whichever happens to be most convenient (Fig. 16). In burning, the phosphorus is of course only uniting with the oxygen of the air; and white clouds of a solid oxide of phosphorus are formed. These dissolve in the water of the dish, and at last the gas remaining in the jar will be approximately pure nitrogen. This may be allowed to stand for further examination. In order to protect the cork from burning with the phosphorus, the latter may rest directly upon a layer of either plaster-of-paris or lime, which will serve as a non-conductor of heat.

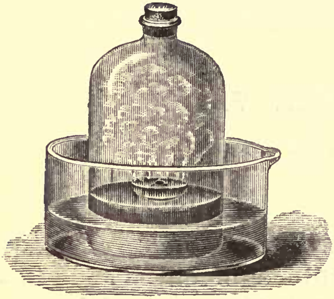

FIG. 16.—Preparation of Nitrogen.

Nitrogen may also be prepared by a sort of reversal of Experiment 20. In that experiment, copper oxide was heated in a stream of hydrogen; water being formed, and metallic copper remaining behind. Now, by heating the copper to redness and passing over it a slow but steady current of air, copper oxide will be reproduced, and only nitrogen will issue from the farther end of the tube. There, by means of a delivery-tube made to dip under water, it may be collected in jars and further investigated. There are several other processes for the preparation of nitrogen, but they need no description here.*

In the free state nitrogen is one of the least interesting of the elements. It is a colorless gas, fourteen times heavier than hydrogen, and having neither taste nor odor. It is incapable of supporting either life or combustion: a lighted candle plunged in it is extinguished; an animal immersed in it immediately dies. Its occurrence in the air, however, shows that it is not poisonous; it kills, not by any deleterious action, but simply because it lacks the power of keeping up the vital processes; when it fills the lungs, the necessary oxygen is excluded.

Nitrogen combines directly with only a very few

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* In short courses of study the experimental preparation of nitrogen may be omitted altogether.

of the other elements, such as boron, silicon, and the rare metals titanium and tungsten. Its important compounds with oxygen, hydrogen, and so on, are all formed by indirect processes, and, as a general rule, are very easily decomposed. Nearly all of the explosive substances practically in use are compounds of nitrogen, and their explosiveness is a consequence of this ready decomposibility. Gunpowder, gun-cotton, nitroglycerine, dynamite, and fulminating powder, are all cases in point.

The composition of air, which may be approximately put at one fifth oxygen with four fifths nitrogen, is more precisely given in the following percentages:

	By weight.	By volume.
Oxygen...........................	23.0	20.8
Nitrogen.........................	77.0	79.2
	100.0	100.0

In a rough way the composition by volume may be verified in a class-experiment, as follows:

EXPERIMENT 22.—Invert a large test-tube, or, better, a graduated tube closed at one end, in a dish containing mercury (Fig. 17). Now melt under warm water a little phosphorus, and take up a drop of it upon the end of a stout wire. When it solidifies, pass the small pellet thus formed under the surface of the mercury and up into the tube. Leave it in position for several hours, or longer if need be. The phosphorus will slowly oxidize, and the mercury will gradually rise in the tube until but four fifths of the original air remains. A lighted match plunged into this remaining gas will be extinguished, showing it to be nitrogen.

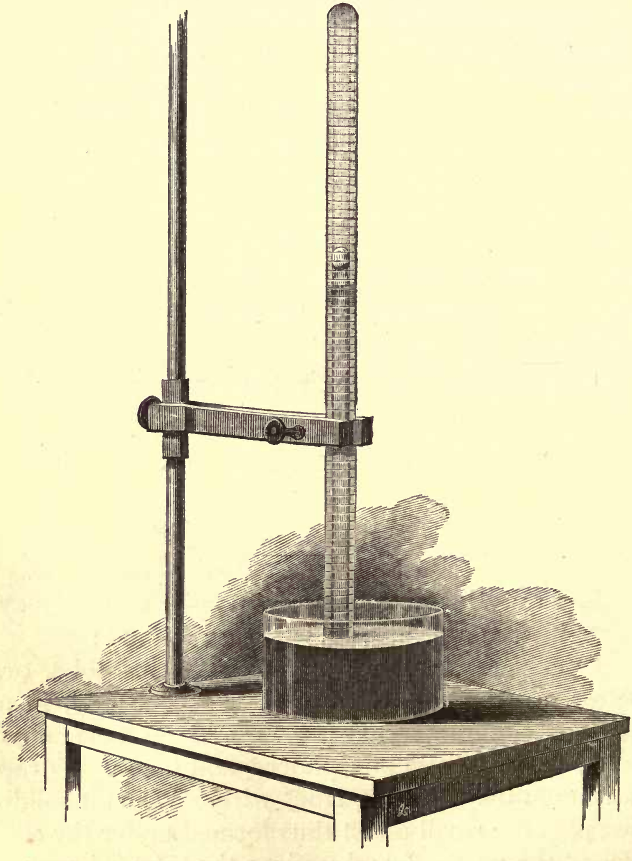

FIG. 17.—Analysis of Air.

Air is only a mixture—not a chemical compound. This will appear more clearly after we study the true oxides of nitrogen in the next chapter. Still, some considerations bearing upon this point may well be offered here. If we artificially mix oxygen and nitrogen gases in the proper proportions, the mixture will have all the characteristic properties of air, and yet none of the usual phenomena which attend chemical union will be manifest. Furthermore, although air is practically constant in its composition, whether taken from the tops of mountains or the depths of valleys, from near the Equator or in the Arctic zone, it does exhibit slight variations which can be detected by refined analyses. Some remarkable experiments by Professor Morley illustrate this fact. It has been supposed by some meteorologists that the sudden periods of severe weather popularly known as "cold snaps" are due to the vertical descent of intensely cold air from very great elevations. Now, oxygen is heavier than nitrogen in the ratio of sixteen to fourteen, and is consequently more powerfully affected by gravitation. There is, therefore, in spite of the ease with which gases diffuse into each other, becoming more and more perfectly mixed, a slight tendency to a concentration of the heavier oxygen near the earth's surface, and a corresponding excess of nitrogen at very great heights above. If, now, a "cold snap" is caused by a sudden descent of air from an exceedingly high level, the air during it should be slightly poorer in oxygen than at other times. This, by a long series of daily analyses of air, Professor Morley finds to be the fact; although the differences are so small as to be comparatively unimportant.

In speaking of *air* we always mean the gaseous mixture above described, which is 14.43 times as heavy as hydrogen. In the *atmosphere* around us, however, several other substances occur, but in widely varying proportions. First, the vapor of water is always present, and plays an important part in determining the character of a climate. Secondly, *carbon dioxide* is invariably to be found, in quantities ranging from three to seven volumes in ten thousand volumes of air. The average amount in the open country is about four volumes; at sea the proportion is less, and near large towns it is greater. Any quantity over seven volumes is decidedly injurious to health. Small as these proportions are, the total quantity of *carbon dioxide* in the atmosphere is enormous; and, as we shall see when we come to study carbon, its influence in connection with the growth of plants is extremely important. Thirdly, ammonia in minute traces is a regular constituent of the atmosphere. This, frequently combined with nitric acid, is brought down to the earth by snow and rain, and serves to supply plants with a considerable part of their nitrogen. All of these ingredients of the atmosphere, and probably also ozone, are essential, and necessary in the economy of nature. With them various accidental impurities are frequently found, products of putrefaction, of combustion, and so on.

CHAPTER VII.

AMMONIA AND THE OXIDES OF NITROGEN.

The compounds formed by the union of nitrogen with hydrogen and oxygen are extremely important and interesting, both from a practical and from a theoretical point of view.

With hydrogen alone, nitrogen combines in only a single proportion; the compound being the well-known substance, ammonia. We have already seen that this body occurs in minute quantities in the atmosphere; it is also found in rain and river waters, and in all fertile soils. It is continually produced in nature by the decomposition of animal matter, and it may be prepared artificially by distilling refuse scraps of horn, hoofs, bones, or hair. In the manufacture of illuminating-gas it is developed from the nitrogen contained in the coal, and it is retained by the water through which the gas is passed on its way to the gas-holders. The ammoniacal solution thus obtained is now the chief commercial source of ammonia. It is first mixed with sulphuric acid, forming a substance known as ammonium sulphate, which is used to some extent as a fertilizer. This compound, heated with lime, evolves ammonia copiously.

Experiment 23.—Rub together in a mortar a fragment of "sal ammoniac" (ammonium chloride), a bit of lime, and a few drops of water. Ammonia will be set free and may be recognized by its smell. All compounds of ammonia behave in the same way; so that trituration with lime affords a ready means of testing for the substance.

Experiment 24.—Pulverize two parts by weight of ammonium chloride and one part of quicklime. Mix, and transfer the mixture to a stout glass flask provided with a delivery-tube (Fig. 18). Upon heating, ammonia will be freely given off, and it can be collected in test-tubes or small bottles inverted over mercury. The usual pneumatic trough or water-pan can not be used in this case, because of the solubility of ammonia in water.

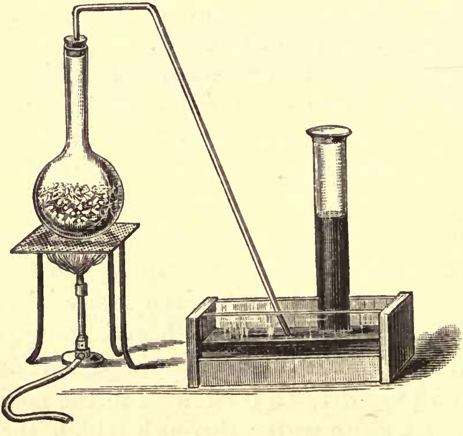

Fig. 18.—Preparation of Ammonia.

Ammonia, thus prepared, is a colorless gas of a peculiar, characteristic, very pungent odor. Under ordinary circumstances it is neither combustible nor a supporter of combustion; but, mixed with a large quantity of oxygen, it may be made to burn with a yellow flame. By weight it is composed of fourteen parts of nitrogen united with three of hydrogen; or, by bulk, one volume of the former gas to three of the latter. These four volumes condense to two in the compound, the ammonia formed being eight and one half times heavier than hydrogen. These figures carry weighty significance, which will appear in the next chapter.

Ammonia is extremely soluble in water, particularly when the latter is cold. At the temperature of 0° C., one cubic centimetre of water will absorb 1,148 c. c. of the gas; while at 15° only 783 c. c. will be taken up. This solubility may be illustrated by introducing a few drops of water into one of the tubes filled with ammonia during Experiment 24, and left in position over mercury. The water will absorb the gas almost instantaneously, and the mercury will suddenly rise to take its place in the tube.

The aqueous solution of ammonia is the common *aqua ammonia*, ammonia-water, or spirits of hartshorn of the shops. The last name reminds us that ammonia was at one time prepared from the horns of deer. Ammonia-water is used to some extent in medicine, and has many important applications in chemical manufactures. It varies much in strength, but it always has the characteristic odor of the gas, and is strongly alkaline. It is also caustic; and, when strong, readily blisters the skin. When boiled, it gives off its gaseous ammonia. The latter, by cold and great pressure, is easily condensed to a colorless liquid, which, when the pressure is released, rapidly evaporates, producing intense cold.

This fact is applied in Carré's machine for making artificial ice.* All ice-machines depend upon the principle that a liquid, in evaporating, absorbs heat from surrounding objects. Liquefied gases evaporate suddenly, and therefore absorb heat suddenly.

With oxygen, nitrogen unites in five different proportions; and two of its oxides combine further with water to form two well-known acids. Since nitric acid is the most convenient starting-point for the preparation of all these other compounds, it may properly be the next substance to engage our attention.

EXPERIMENT 25.—Arrange a retort and receiver as in Fig. 15. Put a weighed quantity of saltpeter (potassium nitrate) in the retort, pour over it an equal weight of strong sulphuric acid, and heat. Nitric acid will distil over; and at last a white solid, potassium hydrogen sulphate, will remain behind.

In the commercial manufacture of nitric acid sodium nitrate is used instead of saltpeter, being cheaper. But any nitrate, distilled with sulphuric acid, will yield nitric acid in the same way. Nitrates are simply the compounds formed by nitric acid with the various metals and bases, and all have names similar to those mentioned above. Sulphuric acid is stronger than nitric acid, and displaces it from its compounds, forming sulphates instead. Such names as silver nitrate, lead nitrate, copper sulphate, and zinc sulphate, are good examples of this kind of nomenclature. Similarly, carbonic acid forms carbonates; boric acid, borates; phosphoric acid, phosphates; acetic acid, acetates, and so on.

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* See "Roscoe and Schorlemmer's Chemistry," vol. i, p. 383; or "Deschanel's Physics," pp. 329–330.

Nitric acid, when pure, is a colorless liquid of specific gravity 1.52. Commonly it is somewhat yellow, from the presence, as an impurity, of one of the oxides of nitrogen. It has a suffocating odor, an intensely sour taste, and is exceedingly corrosive. It attacks all ordinary metals except gold and platinum; and, indeed, dissolves most of them. Hence the early chemists gave it the name of *aqua fortis*, or "strong water." Applied to the skin, it produces yellow stains, which wear off only after several days; and, if strong, it causes corrosion as painful as a burn. Physicians use it somewhat as a caustic; it is employed in etching copper plates for engravings; and it has important applications in refining the precious metals, in making nitroglycerine, gun-cotton, the aniline dyes, and so on. The following experiments with nitric acid will be found instructive:

EXPERIMENT 26.—Cover a piece of bright sheet copper with a thin coating of wax. Scratch a design through the wax with a sharp needle. Now pour over the sheet a little nitric acid, previously diluted with an equal bulk of water, and after a few minutes wash it off again. Upon cleaning off the wax the design will be found to be etched into the copper.

EXPERIMENT 27.—Cover a bit of lead in a glass or porcelain dish with nitric acid diluted as before. Reddish fumes will be given off, and the metal will dissolve. If the solution be allowed to stand for a while, or if it be boiled down somewhat, it will deposit white crystals of lead nitrate.* These can be

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* This experiment may be varied by using other metals than lead and getting other nitrates. Any common metal will do, except tin or

used, if time permits, in a repetition of Experiment 25 for the preparation of nitric acid.

Experiment 28.—Pour dilute nitric acid over a few clippings of quill, bits of white feather, or fibres of white silk. They will be stained permanently yellow.

Experiment 29.—Put a fragment of any nitrate into a test-tube, and dissolve it in the smallest possible quantity of water. Add to the solution, cautiously, an equal bulk of strong sulphuric acid, and allow the mixture, which has become hot, to cool. In another test-tube dissolve with water a crystal of sulphate of iron. Pour this solution, very slowly, into the first test-tube, holding the latter slantwise, so that the two fluids will form two separate layers, without mixing. At the boundary between these layers a brown ring will appear. This is the test by means of which nitric acid and nitrates are ordinarily detected.

In speaking of ammonia it was described as being strongly *alkaline*. Inasmuch as the terms *acid* and *alkaline* will be frequently used in this book, the distinction between them may well be illustrated here.

Experiment 30.—Into one test-tube of water pour a few drops of nitric acid, and into another a little ammonia. Into the one containing the acid dip a slip of blue litmus-paper.* It will become red; and if it be now inserted into the ammonia the

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antimony. These, instead of dissolving, are converted into white, insoluble oxides.

* Litmus is a coloring matter obtained from certain lichens. The juice of the common red cabbage may be used as a substitute for it; being turned green by alkalies and regaining its tint with acids.

blue color will be restored. Blue litmus, then, is reddened by an acid, and reddened litmus is turned blue by an alkali. An alkali is in its chemical properties the opposite of an acid; and in litmus-paper we have a convenient means of recognizing either class of substances.

Any substance which unites with an acid is termed a *base*. The compounds formed are known as *salts*, and, in general, have no effect upon litmus-paper. Strictly speaking, the alkalies are simply the stronger soluble bases, of which soda, potash, and ammonia are the best examples. Lime is also strongly alkaline.*

EXPERIMENT 31.—Put a slip of litmus-paper in a porcelain or glass dish containing ammonia, and add nitric acid cautiously, stirring meanwhile, until the paper is just faintly reddened. Now add a drop of ammonia, then a drop of acid, and so on, until the acid and alkali exactly neutralize one another. Evaporate the liquid, and white crystals will form which are neither acid nor alkaline. They constitute a salt, ammonium nitrate, which may be reserved for use in a future experiment.

The other nitrogen acid previously referred to is unimportant. It contains less oxygen than nitric acid, and is named nitrous acid. The terminations *ous* and *ic* are used in chemical nomenclature to indicate lower and higher degrees of combination respectively. The salts of nitrous acid are called nitrites. So, also, we have sulphurous and sulphuric acids, the one forming sulphites and the other

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* The true significance of the terms acid, alkali, base, and salt will be developed in subsequent chapters. Exhaustive definitions would be inappropriate here.

sulphates. The names of salts derived from *ous* acids end in *ite*, those from *ic* acids in *ate*.

One of the fundamental principles of chemistry is the *law of definite proportions.* This law asserts that *any given chemical compound always contains precisely the same elements in exactly the same proportions.* No variation is possible. When, however, two elements unite to form more than one distinct compound, the *law of multiple proportions* comes into play. This law is best illustrated by the five oxides of nitrogen, which are composed by volume as follows:

Nitrogen	monoxide	contains	2	vols.	nitrogen	with	1	vol.	oxygen.
"	dioxide	"	"	"	"	"	2	"	"
"	trioxide	"	"	"	"	"	3	"	"
"	tetroxide	"	"	"	"	"	4	"	"
"	pentoxide	"	"	"	"	"	5	"	"

We find a similar regularity in their composition by weight:

Nitrogen	monoxide	contains	28	parts of	nitrogen	to	16	of	oxygen.
"	dioxide	"	"	"	"	"	32	"	"
"	trioxide	"	"	"	"	"	48	"	"
"	tetroxide	"	"	"	"	"	64	"	"
"	pentoxide	"	"	"	"	"	80	"	"

In both tables, nitrogen being constant, we see that the oxygen varies in a simple multiple ratio. Hence the law, of which many other examples could be cited, that *when two elements unite to form several compounds, the higher proportions of each are even multiples of the lowest.*

Two of these oxides, the third and the fifth, are unimportant. The fifth is a white, crystalline, explosive body, which reacts with water so as to form nitric acid. From the third, nitrous acid is similarly derived. These two compounds need no further notice here. The others are more important.

Nitrogen monoxide, commonly known as nitrous oxide, is a colorless, odorless, slightly sweetish gas, twenty-two times heavier than hydrogen. By great cold and pressure it can be liquefied, and even frozen solid. The only available mode of preparation is as follows:

EXPERIMENT 32.—Arrange a test-tube and delivery-tube precisely as for the preparation of oxygen. Fill the test-tube half full of dry ammonium nitrate (see Experiment 31), and heat very gradually. The ammonium nitrate will first melt, and then undergo decomposition; the products of the latter change being nitrogen monoxide and water. The nitrous oxide can be collected in a gas-bag, or in bottles over the water-pan. If the heating be conducted too rapidly, the gas will be likely to contain deleterious impurities.

Although nitrous oxide is not really capable of sustaining life, it may be breathed to a limited extent without danger. For this purpose, however, it should be quite pure; a condition best to be secured by using only materials of good quality, evolving the gas very slowly, and washing it by causing it to bubble through several bottles of water before it reaches the gas-bag. When inhaled in small quantities, nitrous oxide produces a peculiar exhilaration, because of which it has received the popular name of "laughing gas." Prolonged inhalation leads to unconsciousness, with complete insensibility to pain. Hence its use by dentists as an anæsthetic.

In nitrous oxide the elements are feebly united. Strong heating, therefore, will decompose it, setting oxygen free. By virtue of this fact it is capable of supporting combustion. Immerse a splinter of ignited charcoal in the gas, and it will burn almost as brilliantly as in pure oxygen. The red-hot coal first decomposes a little of the gas; the oxygen thus liberated takes part in the combustion, developing more heat; this leads to further decomposition, more oxygen becomes free, and so on to the end of the reaction. To verify this point, repeat Experiments 12, 13, and 15, using nitrogen monoxide instead of oxygen.

Nitrogen dioxide, sometimes called nitric oxide, is another colorless gas only fifteen times heavier than hydrogen. Its odor is extremely suffocating, and it supports combustion only in one or two exceptional instances. It is prepared thus:

EXPERIMENT 33.—Put some copper scraps or turnings in the flask previously used for generating hydrogen, and cover them with a half-and-half mixture of nitric acid and water. Connect the delivery-tube with a glass jar *full* of water, and inverted in the usual way over the water-pan. At first, heavy brownish-red vapors will be evolved, but after a few moments they will disappear, and the jar will fill with colorless nitric oxide.

The most interesting property of this gas is its power of absorbing oxygen. Lift the jar just filled with it so as to admit the air, and it will change to the deep-red suffocating gas which was noticed at the beginning of the experiment. This colored gas is nitrogen tetroxide, or hyponitric acid, and we shall frequently encounter it in our experiments.

It appears whenever metals are dissolved or oxidized by nitric acid.

In these experiments we have seen how intimately the oxides of nitrogen are connected, and also that all are derived either from nitric acid or nitrates. We may now go a step further and obtain even the strong base ammonia as a derivative of nitric acid, as follows:

EXPERIMENT 34.—Add some zinc filings to a strong solution of caustic potash, and heat the mixture in a flask, gently. Now put in a little nitric acid, but not so much as to neutralize the alkali. Ammonia will be given off, and it may be recognized by its smell. In this experiment hydrogen is produced by the action of the zinc upon the alkali; and this, at the instant of its liberation, so reacts upon the nitric acid as to transform it into ammonia and water.

CHAPTER VIII.

ATOMIC WEIGHTS AND CHEMICAL FORMULÆ.

In the foregoing chapters we have studied a number of compounds, involving the consideration of only three elements, hydrogen, oxygen, and nitrogen. If, now, we scrutinize their composition a little more closely, some remarkable relations may be brought out.

To facilitate study, let us begin by adopting a set of abbreviations or symbols, by which the various elements may be concisely indicated. Such symbols are a necessity to the chemist, and to each element one is definitely assigned. Thus, H represents hydrogen, O oxygen, N nitrogen, and C carbon. Since several elements may have names beginning with the same initial letter, double letters are frequently employed, as follows:

C represents carbon,
Cd " cadmium,
Ca " calcium,
Cs " cæsium,
Ce " cerium,
Cl " chlorine,
Cr " chromium,
Co " cobalt,
Cb " columbium,
Cu " copper.

The last of these is derived from the Latin *cuprum*. So also we have Fe, from *ferrum*, for iron; Ag, from *argentum*, for silver; Au, from *aurum*, for gold; Sn, from *stannum*, for tin; and so on in several other cases. These symbols should all be learned by actual use, rather than by mere memorizing.*

Now, using these symbols, let us tabulate the compounds thus far examined; giving the composition of each both by volume and by weight:

	By volume.	By weight.
Water.	2 vols. H, 1 vol. O.	2 parts H, 16 parts O.
Hydrogen dioxide.	2 " H, 2 " O.	2 " H, 32 " O.
Ammonia.	3 " H, 1 " N.	3 " H, 14 " N.
Nitrogen monoxide.	2 " N, 1 " O.	28 " N, 16 " O.
" dioxide.	2 " N, 2 " O.	28 " N, 32 " O.
" trioxide.	2 " N, 3 " O.	28 " N, 48 " O.
" tetroxide.	2 " N, 4 " O.	28 " N, 64 " O.
" pentoxide.	2 " N, 5 " O.	28 " N, 80 " O.
Nitrous acid.	1 vol. H, 1 " N, 2 " O.	1 " H, 14 " N, 32 parts O.
Nitric acid.	1 " H, 1 " N, 3 " O.	1 " H, 14 " N, 48 " O.

These numbers are very suggestive, especially when we consider them in the light of the law of multiple proportions. Hydrogen is represented by 1, 2, and 3 volumes, or 1, 2, and 3 parts by weight. Oxygen we find in the proportion of 1, 2, 3, 4, and 5 volumes, or 16, 32, 48, 64, and 80 parts by weight. Nitrogen occurs in 1 and 2 volumes, or 14 and 28 parts by weight. In brief, as far as our experience goes, if we take hydrogen as our standard of comparison and put its combining value at unity, oxygen always combines in the proportion of 16 parts by weight or some even multiple thereof, and nitrogen in the ratio of 14 parts or a multiple. Furthermore,

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* See table of elements in Chapter II.

these numbers, 14 and 16, which we may now call the *combining weights* of nitrogen and oxygen, also represent the specific gravity of these gases, referred to hydrogen as unity.

As we extend our observations to the other chemical elements, we shall find similar relations holding good everywhere. For each element a definite combining weight can be found, which will apply in all the compounds into which the element can enter. For example:

1 part H unites with 35.5 parts Cl.
1 " H " " 80 " Br.
1 " H " " 127 " I.

These values, 35.5, 80, and 127, are the combining weights of chlorine, bromine, and iodine respectively; and they also represent the specific gravity of each element in the gaseous state compared as before with hydrogen as unity.

But many of the elements do not combine directly with hydrogen, and therefore their combining weights need to be determined indirectly. This is easily done through the medium of some other element; thus:

35.5 parts Cl unite with 23 of Na, 39 of K, or 108 of Ag.
80.0 " Br " " 23 " Na, 39 " K, " 108 " Ag.
127.0 " I " " 23 " Na, 39 " K, " 108 " Ag.

Hence 23 may be taken as the combining weight of sodium, 39 of potassium, and 108 of silver; and if we go further and examine the compounds of these metals with oxygen, nitric acid, etc., we shall find that the values here assigned are in perfect harmony with those previously found for hydrogen, oxygen, and nitrogen. The practical importance of such numbers will appear as in subsequent chapters we become familiar with their use.*

Now, what do these simple relations mean? Why do we never find oxygen uniting in fifteen or seventeen parts, but always in proportions represented by multiples of sixteen? The answer to this question was discovered by Dr. John Dalton, of Manchester, England, who put forth in 1808 the atomic theory which lies at the foundations of modern chemistry. If matter is, as we have already supposed, made up of minute, indivisible atoms, it is plain that in chemical union only *whole* atoms and multiples of whole atoms can take part. Fractions of atoms are impossible. If, then, hydrogen and oxygen unite chemically, they must do so in proportions representing either the relative weights of their atoms, or simple multiples thereof, and similar rules must govern the combination of all the elements. We assume, therefore, that the combining weights really represent the relative weights of the different atoms, compared with hydrogen as unity. That is, an atom of oxygen weighs sixteen times as much as an atom of hydrogen, an atom of nitrogen fourteen times as much, an atom of silver one hundred and eight times as much, and so on. These values are called the *atomic weights* of the elements, and a full table of them is given in Chapter II. As to the *real* weights of the atoms we have no definite knowledge; but concerning these *comparative* weights we are quite certain. As we continue our

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* The history of the discovery of the combining weights is admirably given in the earlier chapters of Wurtz's "Atomic Theory" ("International Scientific Series," vol. xxix).

studies we shall find other lines of evidence confirming our present conclusions very strongly.

With the aid of the elementary symbols and atomic weights we are now ready to approach the subject of chemical formulæ. First, let us render our symbols a little more precise. Let H, for example, represent not only hydrogen in general, but exactly one unit weight of hydrogen, or one unit volume, or, more definitely still, *one atom*. Let O, N, C, etc., similarly stand for *one atom* of each element respectively, and for 16, 14, 12, etc., parts by weight, as the case may be. Furthermore, let us express several atoms of an element by numerals added to its symbol; as, for example, H, H_2, H_3, H_4, etc., for one two, three, or four atoms of hydrogen.

Water, as we have already seen, contains two unit weights, or two volumes of hydrogen, combined with sixteen unit weights or one volume of oxygen. Its formula, accordingly, is written H_2O; the symbols being placed side by side to indicate chemical union. Hydrogen dioxide, on like principles, becomes H_2O_2, and the nitrogen compounds are easily formulated as follows:

Ammonia,	NH_3.
Nitrogen monoxide,	N_2O.
" dioxide,	N_2O_2.*
" trioxide,	N_2O_3.
" tetroxide,	N_2O_4.*
" pentoxide,	N_2O_5.
Nitrous acid,	HNO_2.
Nitric "	HNO_3.

These formulæ almost explain themselves. For example, let us consider the last one, because it is

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* These two formulæ should be halved, becoming NO and NO_2 respectively, for reasons which will be presented further on.

the most complicated. It shows, first, that nitric acid contains one atom of hydrogen, one of nitrogen, and three of oxygen combined together; and next, that the gases are united by volume in the same ratio of 1 : 1 : 3. By weight it indicates one part of the first element, fourteen of the second, and three times sixteen of the third. Finally, just as H represents *one atom* of hydrogen, so HNO_3 stands for *one molecule* of nitric acid, and the sum of the *atomic weights* $1 + 14 + 48$, or 63, is called the *molecular weight* of the compound. If we wish to indicate two or more molecules of nitric acid, we may write either $2HNO_3$, or $(HNO_3)_2$; but the former method is customary.

All such formulæ as these are capable of being treated in a somewhat mathematical way, so that chemical reactions may be written out in the form of equations. On one side of an equation we write the formulæ of the substances with which our reaction begins, and on the other the formulæ of the substances produced by the change. Thus, in making oxygen we heat potassium chlorate, $KClO_3$, getting potassium chloride and the gas sought for. The equation is simple:

$$KClO_3 = KCl + O_3.$$

Again, ammonium nitrate, $N_2H_5O_3$, splits up, on heating, into nitrogen monoxide and water, as follows:

$$N_2H_6O_3 = N_2O + 2H_2O.$$

Hydrogen is commonly prepared by the action of sulphuric acid, H_2SO_4, upon zinc; zinc sulphate, $ZnSO_4$, being also formed. This reaction we may write:

$$Zn + H_2SO_4 = H_2 + ZnSO_4.$$

It will be noticed that the plus sign, $+$, is used to indicate addition, or mixture, as distinct from chemical union. The minus sign is sometimes used also, to represent the withdrawal of certain elements from a compound.

This class of chemical equations has very great practical utility, inasmuch as they enable us to calculate the results of reactions in advance. Suppose, for instance, we wish to prepare a definite quantity—say one pound or one kilogramme of nitric acid—and desire to know just how much material to use in order to avoid wasting. The reaction is as follows:

$$KNO_3 + H_2SO_4 = KHSO_4 + HNO_3.$$

That is, one molecule of potassium nitrate and one molecule of sulphuric acid yield one molecule of potassium hydrogen sulphate and one molecule of nitric acid. Now the molecular weight of KNO_3 is $39 + 14 + 48 = 101$; that of H_2SO_4 is $2 + 32 + 64 = 98$; and that of HNO_3 is $1 + 14 + 48 = 63$. Hence, 101 parts of KNO_3, treated with 98 of H_2SO_4, will give 63 parts of HNO_3. For "parts" now read "pounds," "ounces," "grammes," or "kilogrammes," as the case may be, and the problem resolves itself into an easy question in arithmetic.

Again, let us consider the preparation of oxygen, for which the equation has recently been given. The molecular weight of $KClO_3$ is $39 + 35.5 + 48 = 122.5$. Hence, 122.5 parts of $KClO_3$ yield 48 parts of oxygen. Suppose now we wish to make exactly fifty litres of oxygen, measured at 0° and 760 mm. In Chapter III we found the weight of one litre of hydrogen, or *one crith*, to be 0.0896 gramme. A litre of oxygen weighs 16 criths, and therefore fifty litres must weigh 71.68 grammes. Hence, by a simple proportion—

$$48 : 122.5 :: 71.68 : x, \text{ or,}$$
$$O_3 : KClO_3 :: 71.68 : x,$$

in which *x* represents the weight of potassium chlorate needed to prepare the quantity of oxygen sought for. If our oxygen is to be measured at a temperature and pressure other than 0° and 760 mm.—say at 21° and 755 mm.—we must correct the weight of our fifty litres by the aid of the formulæ given in Chapter III. Fifty litres of gas, at 0° and 760 mm., will become at 21° and 755 mm.:

$$\frac{50 \times 760 \times 294}{755 \times 273} = 54.2027.$$

This quantity, 54.2027 litres, weighs the same as before—namely, 71.68 grammes, and fifty litres of the expanded gas will weigh

$$54.2027 : 50 :: 71.68 : x,$$

x being the *corrected* weight of the volume of oxygen desired.

The department of chemistry which deals with these calculations is called *stoichiometry*. Many other stoichiometrical problems will be taken up from time to time as we proceed.*

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* For a good outline of the principles of stoichiometry, see Chapter VI of Cooke's "Chemical Philosophy," new edition, 1881.

CHAPTER IX.

CARBON.

CARBON, one of the most common and most interesting of the elements, is found in nature both free and in a vast number of compounds. It is an important constituent of limestone and many minerals; it forms great beds of coal; it is the element chiefly characteristic of animal and vegetable matter. Chemistry is commonly divided into two great branches—inorganic and organic; the former dealing with substances formed in inanimate nature, the latter with the products of organic life and their derivatives. At present, organic chemistry is usually defined as "the chemistry of the carbon compounds," and as such it might be fairly considered here. For convenience, however, organic chemistry will be discussed separately later on; and in this chapter we may limit ourselves to carbon in some of its inorganic aspects.

Carbon itself is one of the best examples of allotropy, since it occurs in three distinct forms—namely, as diamond, as graphite, and as charcoal. In all of its forms it is tasteless, odorless, infusible, non-volatile, and insoluble. It is, however, combustible; readily so as charcoal, more difficultly in its other modifications. But even the diamond burns in the oxyhydrogen-flame. The atomic weight of carbon is 12.

The diamond is found in India, Borneo, South Africa, and Brazil; and occasionally in North Carolina, Georgia, and California. It occurs in crystals, more or less perfect, derived from the regular octahedron (Fig. 19), and has in its purest state a specific gravity of 3.518. In color it ranges from a pure limpidity well described in the phrase "a gem of the first *water*," through various shades of yellow, blue, green, pink, etc., to black. Generally the colorless stones are most prized, the yellow diamonds being of much less value. Occasionally a blue or green diamond brings an enormous price, for these tints are very rare. The black variety is called *carbonado*, and has a slightly lower specific gravity.

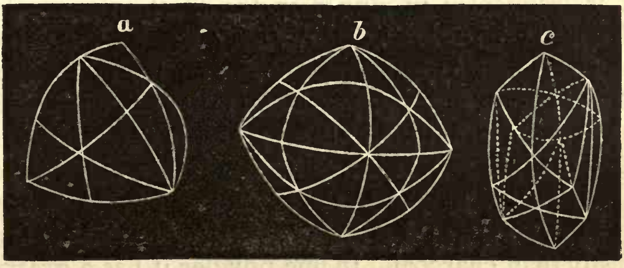

FIG. 19.—Crystals of Diamond.

The diamond refracts light very strongly, and to this property it owes its brilliancy as a gem. It is the hardest of all known substances, and can be cut and polished only with its own powder. Because of its hardness it is used for cutting glass; and the coarser varieties, such as carbonado, serve to tip the diamond-drills which are now employed in rockboring machinery. In 1880 small diamonds were produced artificially by Mr. J. B. Hannay, of Glasgow; but the details of the process have only partially been made public.

Graphite, also known as plumbago or black-lead, is extensively mined in England, Ceylon, Siberia, and California, and at Ticonderoga in New York. There are many other localities in which it is found, so that it may fairly be reckoned one of the commoner minerals. It occurs in some meteorites, and it is frequently produced in the blast-furnace. In the latter case it is dissolved by the molten iron, and crystallizes out upon cooling. It differs from the diamond in many particulars; its color is black, its specific gravity about 2.15, and it crystallizes in six-sided plates. It is a good conductor of heat and electricity, whereas the diamond conducts badly. It may be more easily burned than diamond, less easily than charcoal. In fine powder it has a greasy feel, and is somewhat used as a lubricant for machinery. It is chiefly used in the manufacture of lead-pencils, stove-polish, and crucibles, as a conductor of electricity in the process of electrotyping, and as a glazing for the grains of gunpowder. Gold and silver are usually melted in black-lead crucibles. In the manufacture of coal-gas, a very hard coating of *gas-carbon* is formed in the gas-retorts. This is commonly regarded as a variety of graphite, and is used in the Bunsen galvanic battery, and for making the carbon-points of the electric light.

Amorphous (shapeless or non-crystalline) carbon is always of organic origin. As charcoal it is produced by the imperfect combustion of wood, retaining the structure of the latter almost perfectly. A purer charcoal may be prepared by heating pure white sugar. Another variety, lamp-black, is made by burning tar, rosin, turpentine, or petroleum, with a deficient supply of air, and passing the smoke into large chambers, in which the carbon is deposited. It is simply soot prepared on a large scale, and it is used as a black paint and for making printer's ink. India ink is also made from lamp-black Animal charcoal, as its name suggests, is produced by charring animal matter in close iron cylinders, The finest quality is made from blood, but bone-black, containing with the carbon the earthy constituents of bones, is more extensively prepared.

In all of its varieties amorphous carbon is black, and easily combustible. Its specific gravity ranges from 1.57 to 2.00; the variability resulting from the fact that charcoal is always more or less porous. This porosity confers upon charcoal an extraordinary power of absorbing gases, to which property its value as a disinfectant is due. For example, one cubic centimetre of freshly-burned charcoal will absorb 17.9 cc. of oxygen, 67.7 cc. of carbonic acid, or 171.7 cc. of ammonia. Insert a bit of charcoal in a tube of ammonia-gas filled over mercury, and an immediate rise of the latter in the tube will indicate the absorption. Suppose now that a quantity of charcoal be brought into an atmosphere contaminated with the noxious gases resulting from a leaky sewer or from animal decomposition. They will at once be absorbed; and, coming into close contact with oxygen which has been absorbed also, they will be oxidized and rendered harmless. The vigor of this action may be shown by the following experiment:

Experiment 35.—Heat a fragment of charcoal to redness, so as to expel whatever gases it may contain, and allow it to cool under mercury. Now plunge it into a jar of sulphuretted hydrogen (Chapter XV), and after a few moments transfer it to another vessel containing oxygen. The two condensed gases, meeting in the pores of the charcoal, will unite with such intensity that the carbon will at once inflame.

The same principle may receive a number of other less startling but more practical illustrations. Rub a little powdered charcoal upon tainted meat, and the unpleasant smell will disappear. Water frequently has a fetid odor derived from organic impurities; this may be corrected by simply filtering the water through a thick layer of charcoal. So, also, by charring the lower end of a fence-post or telegraph-post, it may be protected to a considerable extent from rotting.

Charcoal also has a very remarkable power of absorbing coloring-matters and many other substances. Animal charcoal is extensively used in sugar-refineries for decolorizing raw brown sugar and converting it into the finer white varieties. A simple experiment will serve to illustrate this property:

Experiment 36.—Half fill a small bottle with red wine, a solution of indigo, or a solution of cochineal, and add an equal bulk of freshly-burned charcoal-powder. Bone-black is better still if it can be obtained. Shake vigorously, and filter; the filtrate will be colorless or nearly so. Beer or ale, similarly treated, loses both its color and its bitterness. Even a solution of quinine may be rendered nearly tasteless by filtering through charcoal, the quinine being absorbed and retained.

Coke is a variety of amorphous carbon which remains behind after coal has been heated for the manufacture of illuminating gas. Coal itself is very impure carbon, containing various compounds of hydrogen, together with nitrogen, oxygen, sulphur, and the various earthy substances which constitute the ash. It varies much in composition, as the following percentage analyses show : *

	Anthracite.	Soft coal.	Cannel-coal.	Lignite.
Carbon................	92.59	89.33	80.07	66.31
Hydrogen............	2.63	4.43	5.53	5.63
Oxygen...............	1.61	3.25	8.10	22.86
Nitrogen.............	0.92	1.24	2.10	0.57
Sulphur...............	.....	0.55	1.50	2.36
Ash....................	2.25	1.20	2.70	2.27
	100.00	100.00	100.00	100.00

The compounds of carbon with hydrogen, the *hydrocarbons*, are very numerous, and are, in general, of organic origin. Coal-oil and petroleum are variable mixtures of hydrocarbons; and the hydrogen of coal exists partly combined with carbon and partly in the form of water. Since the value of coal for the manufacture of gas depends upon the hydrocarbons which it contains, two or three of these compounds may fittingly be described here, while the others will be considered in connection with organic chemistry, further on.

Methane,† also known as marsh-gas, fire-damp,

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* In Dana's "System of Mineralogy" a large number of coal analyses are given. The variations are extraordinary.

† The naming of the hydrocarbons is somewhat arbitrary. This point will be considered under organic chemistry.

and light carbureted hydrogen, is a colorless gas having the formula CH_4. It burns readily with a bluish-yellow flame, emitting much heat and but little light. In nature it is often produced by the slow decay of dead leaves at the bottoms of stagnant pools; hence the common name, marsh-gas. By stirring up the mud beneath a jar of water inserted in such a pool, the bubbles of gas may be collected and identified (Fig. 20). It also frequently accumulates in coal-mines, forming a dangerously explosive mixture with the oxygen of the air. Such mixtures, ignited by miners' lamps, have caused terrible loss of life. *Fire-damp* is the miner's name for the gas, distinguishing it from the suffocating carbonic acid, or *choke-damp*. It sometimes issues in great quantities from the earth, and particularly from artesian wells sunk in search of petroleum. In some such

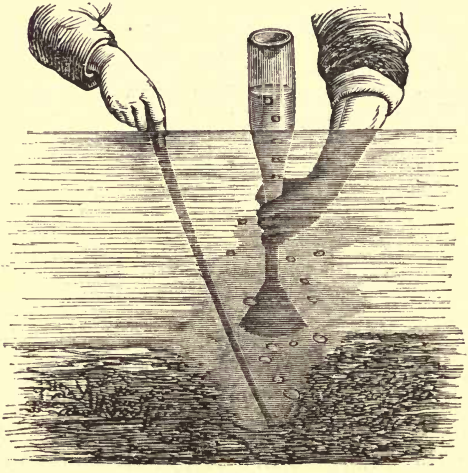

FIG. 20.—Collection of Marsh-gas.

places it serves as a fuel, for driving steam-engines; and the town of Fredonia, New York, is mainly lighted by gas of natural origin, Methane is artificially prepared as follows:

EXPERIMENT 37.—Mix thoroughly two parts of crystallized sodium acetate, four parts of caustic soda, and eight parts of powdered quicklime. Heat gently on an iron plate until the mixture is thoroughly dry and crumbly. Then heat it strongly in a glass tube, such as was used for the preparation of oxygen, and collect the gas over water. Test its inflammability as in the case of hydrogen. In this experiment the lime merely serves to render the mass more porous, and to protect the glass from excessive corrosion by the caustic soda.*

Ethylene, C_2H_4, is another gaseous hydrocarbon of great importance. It is fourteen times heavier than hydrogen, whereas the density of methane is only eight. Hence the old names of *heavy* and *light carburetted hydrogen* respectively. It is easily prepared by heating together alcohol and strong sulphuric acid, and it burns with a luminous, smoky flame. It is also known as ethene and as olefiant (oil-producing) gas. The last name was given it because it unites directly with another gas, chlorine, to form an oily liquid.

Acetylene, C_2H_2, is another gas, of a disagreeably pungent odor, which is formed by the direct union of its elements. When a series of powerful electric sparks are passed between two carbon-points in an

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* A cheaper way of preparing impure methane is to soak lumps of lime in vinegar, and then to heat, as above, the mixture of lime and calcium acetate thus obtained. In this process a good deal of steam is first given off.

atmosphere of hydrogen, acetylene is produced. It combines directly with hydrogen to form ethylene; thus: $C_2H_2 + H_2 = C_2H_4$. It also unites with certain metals, such as copper or silver, yielding explosive compounds of considerable interest. It burns with a blue flame. All the hydrocarbons burn more or less readily, and all form upon complete combustion only carbonic acid and water. For example:

$$CH_4 + O_4 = CO_2 + 2H_2O.$$
$$C_2H_4 + O_6 = 2CO_2 + 2H_2O.$$
$$C_2H_2 + O_5 = 2CO_2 + H_2O.$$

By the imperfect combustion of hydrocarbons, acetylene is often produced; for example, when a candle burns with a smoky flame its peculiar odor may be detected.

Ordinary illuminating gas, distilled from coal, is essentially a mixture, more or less impure, of hydrogen, carbon monoxide, methane, and ethylene. Its production on a small scale may be illustrated by an easy experiment.

EXPERIMENT 38.—Fill the bowl of a common clay tobacco-pipe with powdered soft coal, and cover the latter tightly with a plug of clay. Heat the bowl to redness over a Bunsen gas-flame or between the bars of a grate. Gas will issue from the stem, where it may be ignited.

In manufacturing gas on a large scale, bituminous or cannel coal is heated in retorts of fire-clay or fire-brick which hold from one to two hundred pounds at a time. Several retorts are heated at once over a single fire, and the products of distillation pass out into a series of pipes in which water, coal-tar, ammonia, etc., are deposited. The tar and ammonia, being valuable, are thus saved. Twenty-five years ago the tar was worthless; now it serves as a source of benzene, and of the superb aniline dyes. The gas itself still contains a number of objectionable impurities, which are removed by passing it over some absorbent substance, such as slaked lime.* Different samples of gas differ widely in composition; the differences depending upon the quality of the coal employed, the degree of heat applied to the retorts, and so on. In percentages, the following figures may represent a fair average:

Hydrogen,	50
Methane,	35
Carbon monoxide,	7
Ethylene,	3
Several impurities,	5
	100

In Germany, gas is sometimes distilled from wood; and in our own country there are processes in use which generate hydrogen from steam and charge it with vapors from petroleum. The latter give its flame illuminating power. In ordinary gas the illuminating value depends mainly upon the ethylene which it contains.

If we study a gas-flame closely we shall find that its structure illustrates some important facts relating to the mechanism of combustion. In a common burner the gas issues from a fine jet, and is ignited in contact with a moderate amount of air (Fig. 21). Near the jet we have a stream of gas not yet burned; and here the flame is comparatively cool and non-

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* A good account of the manufacture and purification of coal-gas is given in Roscoe and Schorlemmer's "Treatise on Chemistry," vol. i, pp. 683–704.

luminous. Insert a piece of slender glass tubing at this part of the flame, and the unburned gas may be drawn off and kindled at the farther end (Fig. 22). Above, and somewhat around this darker base, we have the luminous portion of the flame; and here the light is partially due to imperfect combustion. Hold a piece of cold porcelain over the jet for a moment, and soot (that is, carbon) will be deposited upon it. It is these *solid* particles in the flame which become heated and luminous, and they result from the partial combustion of ethylene and some of its related hydrocarbons. Methane yields no free carbon under like circumstances, and of course hydrogen does not; hence their flames, containing only gaseous matter, are non-luminous.* If we do any-

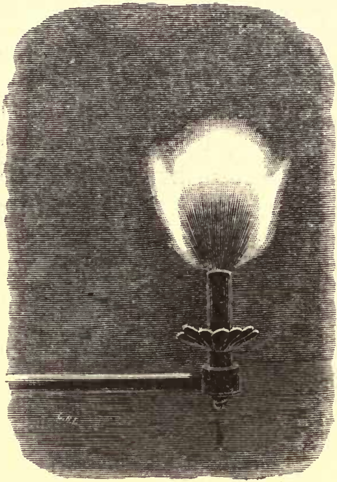

FIG. 21.—Structure of Common Gas-flame.

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* In Experiment 7 the luminosity of a hot solid in a hydrogen-flame was illustrated.

thing to cut off the supply of air from a flame, it will become fuller of carbon-particles and more smoky; a fact which may easily be verified by sliding a piece of sheet-iron or other convenient solid over the top of a gas or kerosene lamp-chimney. As the air is

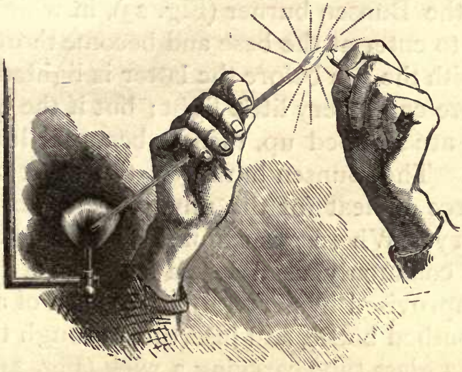

FIG. 22.—Withdrawal of Gas from a Flame-centre.

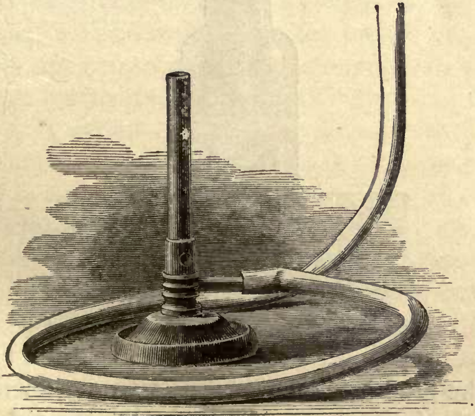

FIG. 23.—Bunsen Burner.

gradually excluded, smoke and soot will form copiously. Conversely, if we render combustion more perfect, and so prevent the deposition of carbon, a flame will become hotter but less brilliant. This is done in the Bunsen burner (Fig. 23), in which air is allowed to enter at the base and become thoroughly mixed with the gas before the latter is lighted. The flame here emits very little light; but if the holes at the base are stopped up, then it becomes luminous as usual. The Bunsen burner is the most convenient source of heat for the minor operations of the laboratory. Where gas can not be had, an alcohol lamp is commonly used instead. Such a lamp is easily improvised by perforating the cork of a small, wide-mouthed bottle, and inserting through the perforation a glass tube carrying a wick (Fig. 24).

FIG. 24.—Improvised Spirit Lamp.

In the mouth blow-pipe we have another illustration of the foregoing principles. By the aid of this little instrument air is blown from the cheeks into a flame, and the latter is rendered much hotter (Fig. 25). Here, again, the flame may be divided into two chief parts; an inner blue cone and an outer portion. The greatest heat is at the apex of the inner flame. A bit of tin or zinc, heated in the outer part of the jet, is first melted and then converted into oxide; hence the name of *oxidizing flame*. On the other hand, the oxide so formed, if heated in the inner cone, will be reduced to the metal again, giving up its oxygen to assist in the burning of the carbonaceous matter there found. This part of the jet, therefore, is called the *reducing flame*. Both parts of the flame are important agents in blow-pipe analysis; and a little practice in heating bits of copper, tin, zinc, lead, etc., supported on pieces of charcoal, first in one and then in the other, will make the relations of the two very clear. The stream of air from the blow-pipe should be made as steady as possible; and one can easily learn to blow lightly from the muscles of the cheeks for several minutes at a time without interrupting respiration. The flame

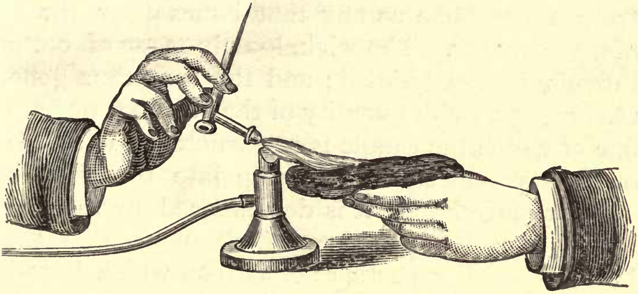

FIG. 25.—Use of Blow-pipe.

of a lamp burning some animal or vegetable oil (lard, whale, or rape-seed oil, for examples), is best for blowpipe work; but alcohol or gas may be used. Kerosene is unavailable, because the chimney interferes.

In a strictly scientific sense a candle-flame is as truly a gas-flame as any that issues from the tip of a gas-burner. The wick, loosely made of cotton threads, is first kindled; and the heat thus generated melts a small quantity of the fat, wax, or paraffine of which the candle is constructed. The liquid oil thus produced is drawn up into the wick by capillary attraction; it is decomposed by the heat, and the *gaseous* products of decomposition then burn, depositing particles of carbon which become luminous. These may be collected as soot; and by means of a glass tube the gas from the center of the flame can be drawn off and ignited. If a sheet of clean white cardboard be suddenly pressed down upon a candle-flame and then withdrawn, it will be found scorched in a ring, thus showing that at the center of the flame there was no active combustion.

When bituminous coal is burned in a furnace, the laws of combustion should be carefully considered. A smoky chimney always means imperfect combustion and waste of carbon; and smoke-preventing appliances, the so-called "smoke-consumers," are getting to be more and more used in cities where soft coal is the chief fuel. Many such appliances have been patented, but all aim at the same result—namely, to bring about perfect combustion. Sometimes, fine jets of steam are blown into the furnace. These are decomposed at first, yielding oxygen and hydrogen, which serve to make the fire more intense. In other cases the coal is applied in such a way that the smoke from the fresh portions of fuel is conducted over glowing beds of coke, the latter being merely the earlier charges from which the sooty hydrocarbons have been burned away. In some metallurgical furnances the fuel is rendered gaseous at the start, and the gases are then burned with abundance of air. Such furnaces give great heat and waste little or no fuel.

For every combustible substance there is a definite temperature below which it will not ignite. If a flame be cooled below the ignition-point of the gas which forms it, it will go out. Press a piece of wire gauze down upon a gas-flame, and the latter will be flattened ; it can not penetrate the metallic net-work. The gas itself passes through, but the wire has conducted so much heat away from it that combustion is no longer possible. You can hold the gauze over a jet of gas and kindle the latter above, but the flame can not then descend to the burner. Or, you may hold two pieces of gauze parallel to each other over a stream of gas, and produce a flame between them which shall be unable to pass either above or below. These facts find their application in the safety-lamp of Sir Humphry Davy (Fig. 26). This, which was invented for the protection of coal-miners against fire-damp, is merely a lamp inclosed in a netting of fine-wire gauze. This inclosure may be filled with flame, but the latter can not penetrate its prison-walls and ignite the explosive gaseous mixture without.

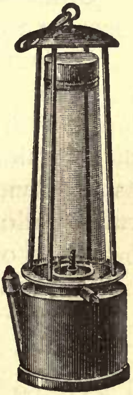

FIG. 26.—Davy's Safety-Lamp.

CHAPTER X.

CARBON—(*continued*).

CARBON unites with oxygen in two proportions, forming a monoxide, CO, and a dioxide, CO_2.

Carbon monoxide, more commonly known as carbonic oxide, is a colorless, odorless gas which burns with a blue flame. It is not produced by the direct union of its elements; for when carbon, either as diamond, graphite, or charcoal, is burned, only carbon dioxide is formed. By passing the latter, however, over red-hot coals, half of its oxygen may be withdrawn, and carbon monoxide results from the change:

$$CO_2 + C = 2CO.$$

This often happens in coal-stoves and furnaces, especially in the blast-furnace; carbon dioxide being produced by the combustion of the lowest layer of fuel, and rising through the glowing coals above. The blue flames which play over the surface of an anthracite-fire are due to carbon monoxide, and the product of the combustion is CO_2:

$$CO + O = CO_2.$$

Carbon monoxide may be artificially prepared by various processes; but most conveniently by heating either crystallized oxalic acid or potassium ferrocyanide with strong sulphuric acid. By the reaction which ensues, both oxides of carbon are formed; but, by passing the mixed gases through a solution of caustic potash, the dioxide may be absorbed, leaving the monoxide pure.

The preparation of carbon monoxide should be undertaken only with extreme care, because the gas is dangerously poisonous. A trace of it in the air we breathe will produce headache and dizziness, and anything over one percent admixture might prove fatal. It sometimes escapes from badly-constructed stoves into improperly-ventilated rooms, and causes serious annoyance. Cheap cast-iron stoves are especially liable to work this kind of mischief, and deaths have resulted from the careless use of such stoves in close sleeping-apartments. All illuminating gas made from coal contains carbon monoxide as one of its ingredients.

The other oxide of carbon, carbon dioxide, is met with under a great variety of conditions. We find it ever present in the atmosphere; it is always produced when carbon or compounds of carbon are burned; we exhale it from our lungs; it is evolved from decaying animal and vegetable matter; and we recognize it among the products of fermentation.

EXPERIMENT 39.—Cover the bottom of a glass jar with lime-water,* and suspend over it a burning bit of candle. Close the jar, and the candle will soon burn itself out. Now shake vigorously, and the lime-water will become milky. Upon standing,

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* Prepared by stirring powdered lime into water, leaving the mixture to stand for at least an hour, and then filtering. The solution should be perfectly clear.

the milkiness will be deposited as a white sediment. This sediment is calcium carbonate (carbonate of lime), and its formation proves the presence of carbon dioxide in the air of the jar. A piece of wood or charcoal burned in place of the candle will give the same result.

EXPERIMENT 40.—Pour some lime-water into a tumbler, and through a piece of glass tubing blow air into the liquid for several minutes from the lungs. The lime-water will become milky, showing that carbon dioxide has been exhaled.

EXPERIMENT 41.—Mix in any convenient vessel some very sweet molasses-and-water with a little yeast. Fill a test-tube with the mixture, invert it in the liquid, and let the whole stand in a warm place overnight. Fermentation will occur, and bubbles of carbon dioxide will rise into the tube. Close the mouth of the latter with the thumb, remove it from the vessel, and shake up its gaseous contents with lime-water.

EXPERIMENT 42.—In the same flask and apparatus which previously served for the preparation of hydrogen, put some fragments of chalk, limestone, or marble, and pour over them a quantity of dilute hydrochloric or sulphuric acid. Gas will be given off with brisk effervescence; and by passing a few bubbles of it into lime-water it may be identified as carbon dioxide. Collect the remainder of the gas as usual in bottles or jars over the water-pan.

The last experiment illustrates the only method by which carbon dioxide is practically prepared for use in the laboratory, The limestone, chalk, or marble is calcium carbonate, $CaCO_3$; and the reaction, when sulphuric acid is used, is as follows:

$$CaCO_3 + H_2SO_4 = CaSO_4 + H_2O + CO_2.$$

That is, calcium carbonate, treated with sulphuric acid, yields calcium sulphate, carbon dioxide, and water. Any other carbonate will give a similar reaction with any strong acid, and carbon dioxide will be evolved in the same way. For example, pour vinegar (acetic acid) over common saleratus (a carbonate of sodium), and note the effervescence. As the name indicates, a carbonate is a salt formed by carbonic acid with a base. Since carbonic acid is a very weak acid, any stronger acid can expel it from its salts, as in the foregoing reactions. When free, its formula should be H_2CO_3, but it is incapable of existing independently, and therefore splits up at the moment of its liberation into carbon dioxide and water, $CO_2 + H_2O$. Many carbonates are easily decomposed by heat; for instance, lime, which is calcium oxide, is made by burning limestone in a kiln, when carbon dioxide is evolved freely:

$$CaCO_3 = CaO + CO_2.$$

The lime and carbon dioxide thus separated can be made to unite again only through the intervention of water; the necessary reaction being one which we have already observed in several experiments. Filter off some of the sediment formed by carbon dioxide in lime-water, and test it with a drop of any common acid. It will effervesce, thereby revealing its character as a carbonate. Carbon dioxide is frequently miscalled carbonic acid; indeed, "carbonic-acid gas" is the commonest of its names.

Carbon dioxide is a colorless, odorless gas, which by cold and pressure may be easily condensed to a liquid. When the latter is allowed to escape from a fine jet a part of it evaporates instantaneously, absorbing enough heat from the remainder to freeze it into a white, crystalline solid, like snow. The temperature of this solid is about − 78° C., and if it be pressed between the fingers it produces a painful blister, and sensations like a burn.

Carbon dioxide dissolves to a considerable extent in water, especially under pressure. Some natural waters, from so-called mineral springs, are heavily charged with it, and effervesce upon exposure to the air. The Saratoga and Seltzer waters are good examples. Soda-water is merely water artificially charged with carbon dioxide; and to the same gas champagne owes its sparkle and beer its foam. By standing in the open air these drinks soon lose their gas, and become flat and valueless.

In the chemistry of cooking, carbon dioxide plays an important part. As evolved by yeast it makes bread light and porous; and the same end is attained less wholesomely and perfectly by the aid of saleratus and baking-powders. All the latter preparations owe their value to the carbon dioxide which they are capable of developing; and all leave residues behind which render bread inferior in quality.

Like nitrogen, carbon dioxide is incapable of sustaining either combustion or life. It is not in any sense poisonous, like the monoxide—it is simply inert. We throw it off from our lungs, and replace it with fresh oxygen; it is no longer fit for breathing.

Experiment 43.—Lower a lighted candle into a jar of carbon dioxide. The flame will at once be extinguished. Chemical fire-engines are simply machines which generate carbon dioxide, and throw it, mixed with water, upon fires.

Carbon dioxide sometimes accumulates in old wells, vaults, and cisterns, and in the great vats of breweries; and the workman who descends into such a place to clean it out may in consequence be suffocated. Many fatal accidents of this kind have happened; so that it is always best, before entering a place where carbon dioxide may be, to lower into it a lighted candle. If the latter burns, the air is fit to breathe; if it goes out, then let the place be thoroughly ventilated. The gas also collects at times in unused galleries of coal-mines, where it is known to the miners as choke-damp. In some places it issues in quantity from crevices in the earth, as at the Grotto del Cane* in Italy. Here it forms a layer on the bottom of a small cave; a man, entering, has his head above the level of the gas, and does not notice it; but a dog, carried in by the guide, when placed upon the floor, is immediately overcome.

The fact that carbon dioxide is about half as heavy again as air may easily be illustrated by experiment.

EXPERIMENT 44.—Slowly invert a jar of the gas a short distance above the flame of a candle. The latter will go out, showing that carbon dioxide descends. So, also, we may pour the gas from one vessel to another, almost as if it were a liquid.

EXPERIMENT 45.—Put two glass jars in the pans of a pair of scales, and balance them nicely against each other. Pour carbon dioxide into one of the jars and the latter will sink, having become the

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* Grotto of the Dog.

heavier (Fig. 27). The actual density of the gas, referred to hydrogen as unity, is 22; that of carbon monoxide is 14.

In its relations to the atmosphere, and through

FIG. 27.—Weighing Carbon Dioxide.

the atmosphere to life, carbon dioxide is a substance of the greatest importance. Were its proportions to be but moderately increased, all animals would die; were it wholly withdrawn, vegetable life would perish. Fortunately, its quantity in the atmosphere varies but little, in spite of the fact that every fire and every breathing animal withdraws oxygen from the air and replaces it with carbon dioxide. How is the balance preserved?

In organized life we have a steady circulation of carbon. Directly or indirectly, all animals depend upon vegetable food, the carbon of which becomes a part of the animal tissues. These undergo, through the medium of the lungs, a sort of slow combustion, whereby the animal heat is kept up, and in consequence of which the carbon is converted into carbon dioxide and thrown off into the outer air. Now comes into play one of the most remarkable functions of plant-life: the plant which furnishes the animal with food, in turn seizes upon the carbon dioxide which the latter has rejected, and reconverts its carbon into vegetable tissue. The leaf, in presence of sunlight, decomposes carbon dioxide, retaining its carbon and setting the oxygen free. Without the help of the sunbeam this work could not be done; during the night the leaves rest from their labors. In the manner thus briefly outlined, the plant and the animal balance each other in Nature, and help to keep even the proportion of carbon dioxide in the air.

With nitrogen, carbon forms one compound—a colorless gas, having an odor suggestive of peach-kernels, and burning with a beautiful purple flame. Its formula is C_2N_2; and its name, *cyanogen*, is derived from two Greek words which indicate that it forms some compounds which are blue. Prussian blue is one of them. It unites with metals just as if it were an element, forming salts which are known as *cyanides*. Compounds which thus behave like elements are not infrequent, and are called *compound radicles*. In the present case the true compound radicle, however, is the half of C_2N_2, or CN, which does not exist in the free state, but only in cyanides, such as potassium cyanide, KCN, and so on. Sometimes the CN group is represented by an abbreviated symbol, Cy; and on this plan free cyanogen would be written Cy_2. Hydrocyanic acid, popularly called prussic acid, has the formula HCN. It is one of the deadliest poisons. Cyanogen and its derivatives are best studied among organic compounds, since they are commonly of organic origin. Their further consideration, therefore, must be deferred to the proper chapter.

CHAPTER XI.

COMBINATION BY VOLUME.

We have already noticed the fact that the numbers 14, 16, 35.5, 80, and 127 represent not only the atomic weights of N, O, Cl, Br, and I respectively, but also the relative weights of equal volumes of these elements, in the condition of gas or vapor, compared with hydrogen as unity. In general, with a very few exceptions to be noted hereafter, the atomic weight of an element expresses also its vapor density.

In carbon, however, we meet with an element which does not readily vaporize, so that we can not directly test the accuracy of the foregoing statement with regard to it. Its atomic weight being 12, its vapor should be just twelve times heavier than hydrogen; but whether it is or not we are unable to experimentally determine. We may, nevertheless, study some of the gaseous *compounds* of carbon, and see whether they can shed any light on the subject. Or, in more general terms, we may try to discover whether any simple relation connects the density of a compound gas with the densities of the gaseous elements contained in it.

If we refer back to the chapter upon atomic weights, we shall see that the elementary gases hydrogen, oxygen, and nitrogen, combine by volume in very simple ratios. A few of these may well be reconsidered here, with the addition of figures showing the volumes of the resulting compounds in the state of gases or vapors:

2	vols.	H	with	1	vol.	O,	in all	3	vols.,	form	2	vols.	H_2O.
3	“	H	“	1	“	N,	“ “	4	“	“	2	“	NH_3.
2	“	N	“	1	“	O,	“ “	3	“	“	2	“	N_2O.
2	“	N	“	3	“	O,	“ “	5	“	“	2	“	N_2O_3.

In short, in each of these cases, the elements unite with condensation, and *two* volumes of a compound result. So also with nitric acid, HNO_3, in which five volumes of H, N, and O condense to *two* volumes of the compound vapor. In hydrochloric acid, HCl, a substance to be described in a future chapter, we have an example of a simpler kind. One volume of H unites with one volume of Cl *without* condensation, and here again *two* volumes of the compound gas, HCl, are formed.

From these data, or rather from the *two-volume law* in general, we can easily calculate the density of any compound gas. For example, steam is formed by the union of two unit volumes of hydrogen, weighing two combining units, with one volume of oxygen which weighs sixteen. The resulting two volumes of course weigh eighteen units, and one volume weighs half as much, or is nine times heavier than hydrogen. Hence we may say that *the density of a compound gas or vapor, compared with hydrogen as unity, is half its molecular weight.*[*] Thus—

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[*] To find the density referred to *air* as unity, divide the values given according to this rule, by 14.43. Why?

HCl.	Mol.	weight,	$1 + 35.5 = 36.5$.	Density,	18.75.
H_2O.	"	"	$2 + 16 = 18$.	"	9.
H_3N.	"	"	$3 + 14 = 17$.	"	8.5,
N_2O.	"	"	$28 + 16 = 44$.	"	22.
N_2O_3.	"	"	$28 + 48 = 76$.	"	38.
HNO_3.	"	"	$1 + 14 + 48 = 63$.	"	31.5.

We may now apply this rule to the carbon compounds, *assuming* the density of carbon vapor to be 12, and see whether the results obtained are correct:

CH_4.	Mol.	weight,	$12 + 4 = 16$.	Density,	8.
C_2H_4.	"	"	$24 + 4 = 28$.	"	14.
C_2H_2.	"	"	$24 + 2 = 26$.	"	13.
CO.	"	"	$12 + 16 = 28$.	"	14.
CO_2.	"	"	$12 + 32 = 44$.	"	22.
C_2N_2.	"	"	$24 + 28 = 52$.	"	26.

These densities exactly agree with the results which have been reached by direct experiment. Hence we may conclude that just as 16 represents the density of oxygen, so also 12 stands for the density of carbon in its gaseous compounds; and the more we study the latter the stronger the evidence will become. In a similar way we can investigate the volatile compounds of other non-volatile elements, and prove that the two-volume law above indicated is of universal application. The seeming exceptions to it will be explained in another chapter.

Among the carbon compounds cited above are three which deserve further consideration at this point. Each of the formulæ C_2H_4, C_2H_2, and C_2N_2 is capable of being halved, and the simpler formulæ CH_2, CH, and CN will represent just as well the composition of these substances by weight. CH_2 indicates precisely the same ratio between C and H as the more complex formula C_2H_4; why, then, should we not by preference adopt it? Simply because the density of the gas, doubled, gives us its molecular weight, and the latter agrees only with the higher formula. So also with the other cases. C_2H_4 is one of a series of hydrocarbons—C_2H_4, C_3H_6, C_4H_8, C_5H_{10}, etc.—in which the relative proportions of hydrogen and carbon do not vary. But in vapor density these substances differ widely, and from it, as well as from other evidence to be considered under organic chemistry, we deduce the formulæ given above. In short, the same kinds of atoms may combine in the same relative proportions so as to form many different molecular groups or compounds having different vapor density. If by experiment we ascertain the latter, we are able in any given case to assign a correct molecular weight, and from that to draw conclusions as to the proper formula.

Two of the oxides of nitrogen will illustrate the application of these principles still further. In a previous chapter we gave them provisionally the formulæ N_2O_2 and N_2O_4, so as to bring out more clearly the law of multiple proportions. Properly, however, these particular compounds should be represented by the formulæ NO and NO_2 respectively. If the formula of the first were N_2O_2, its density would be 30; whereas experiment shows it to be only 15. Accordingly, we halve the formula, and so get at the true molecular weight. So also with the other oxide.

The more we study the properties of gases, the more we shall be impressed with the simplicity of the laws which govern them. They expand equally by heat, and are affected equally by pressure; and between the molecular weight and the density we have just recognized a very close relation. All these regularities, with others which fall without the scope of this book, suggest a general law for gases, and such a law was announced by the Italian physicist, Avogadro, in 1811. It may be stated as follows:

Equal volumes of gases, compared under identical conditions of temperature and pressure, contain equal numbers of molecules.

This law may be deduced both from chemical and physical evidence, and has strong mathematical foundations; accordingly, it is accepted by chemists and physicists alike. We, however, need to consider it only in its chemical bearings, and in addition to what has already been said, especially with regard to the difference between atoms and molecules.

So far, our standards of comparison have been the *atom* of hydrogen for atomic and molecular weights, and the unit volume of hydrogen for volumes. Using these standards, we have found that for all the elementary gases so far studied, density and atomic weight have both been represented by the same number; which shows that equal volumes of H, N, O, etc., *contain equal numbers of atoms.* For, if an atom of O is sixteen times heavier than an atom of H, and a litre of O sixteen times heavier than a litre of H, then the litre of O and the litre of H must contain precisely the same number of atoms. With compound gases, on the other hand, a different relation holds; and, as we have seen, the molecular weight is not equal to, but double, density. The reason for this difference is, that we have been comparing molecules with atoms; whereas, in order to verify Avogadro's law, we should compare molecules only with each other.

If, now, we assume that the molecule of hydrogen consists of two atoms, with a molecular weight of two, and represent in a like manner the molecules of the other elements by OO, NN, Cl_2, Br_2, I_2, etc., we shall find that both elements and compounds will come simply and regularly under Avogadro's law. Then, for every gas or vapor, elementary or compound, the density will be one half the molecular weight; a ratio which is due to the fact that the half-molecule, or atom of hydrogen, is taken as our standard of comparison.

But the molecule of an element is not necessarily a double atom. The density of ordinary oxygen, for example, is 16; while that of allotropic oxygen, or ozone, is half as heavy again, or 24. We have here two different molecular groups formed by the same kind of atom; and if the molecule of oxygen is O_2, then the molecule of ozone must be O_3, with a molecular weight of 48. With mercury and cadmium, the vapor density is half the atomic weight; hence the latter is identical with the molecular weight, and the single atom and the molecule are the same. Phosphorus and arsenic, on the other hand, form vapors twice as heavy as their atomic weights would indicate, and their molecules therefore contain four atoms. These points will be considered more fully when we come to describe these elements.*

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* Fuller discussion of the points brought forward in this chapter may be found in Cooke's "Chemical Philosophy," Cooke's "New Chemistry," Wurtz's "Atomic Theory," or Remsen's "Theoretical Chemistry."

CHAPTER XII.

VALENCY.

If we examine the formulæ of many chemical compounds, we shall at first be struck with the great diversity of character among them; but, upon a closer inspection, certain remarkable regularities, of great theoretical importance, will appear. Let us begin with some of the compounds of hydrogen:

I.	II.	III.	IV.
HF.	H_2O.	H_3N.	H_4C.*
HCl.	H_2S.	H_3P.	H_4Si.
HBr.	H_2Se.	H_3As.	
HI.	H_2Te.	H_3Sb.	

Here we have fifteen elements, which unite with hydrogen in such manner as to fall into four well-defined natural groups. These suggest the following considerations:

Every elementary atom has a definite capacity for uniting with other atoms, which we may call its *valency*.† Let us again take hydrogen as our standard of comparison, and assume its valency to be unity. Then the elements in the first column of

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* This particular hydrocarbon is given here because it contains a higher proportion of hydrogen than any other.

† Also called by various writers "valence," "quantivalence," or "atomicity."

the table, which unite atom for atom with hydrogen, may be called *univalent*, those which take two atoms of hydrogen *bivalent*, and those in the third and fourth columns *trivalent* and *quadrivalent* respectively. The atoms themselves, with reference to their valency, may be concisely termed *monads*, *dyads*, *triads*, and *tetrads*—these names being derived from the Greek numerals. Later on we shall meet with *quinquivalent* and *sexivalent* elements, whose atoms are called *pentads* and *hexads* respectively.

The proportions in which atoms combine together depend upon valency. Thus, one monad can unite with one monad, one dyad with two monads, one triad with three monads, and one tetrad with four monads. This is shown in the foregoing table, and also in the following formulæ. The Roman numerals serve to indicate the valency of the several elements:

$K^{i}Cl^{i}$.	$K^{i}Br^{i}$.	$Na^{i}F^{i}$.	$Ag^{i}I^{i}$.
$Cl_2^{i}O^{ii}$.	$Ag_2^{i}O^{ii}$.	$Na_2^{i}S^{ii}$.	$K_2^{i}S^{ii}$.
$P^{iii}Cl_3^{i}$.	$As^{iii}Cl_3^{i}$.	$Sb^{iii}Br_3^{i}$.	$Bi^{iii}I_3^{i}$.
$C^{iv}Cl_4^{i}$.	$C^{iv}Br_4^{i}$.	$Si^{iv}F_4^{i}$.	$Si^{iv}I_4^{i}$.

Again, one dyad unites with one dyad, two triads with three dyads, and one tetrad with two dyads, thus:

$Ca^{ii}O^{ii}$.	$Ba^{ii}S^{ii}$.	$Zn^{ii}O^{ii}$.	$Hg^{ii}S^{ii}$.
$B_2^{iii}O_3^{ii}$.	$N_2^{iii}O_3^{ii}$.	$Sb_2^{iii}S_3^{ii}$.	$Bi_2^{iii}S_3^{ii}$.
$C^{iv}O_2^{ii}$.	$C^{iv}S_2^{ii}$.	$Si^{iv}O_2^{ii}$.	$Si^{iv}S_2^{ii}$.

In each of these cases the valencies of one element exactly balance those of the other. Some of the symbols used belong to metals which do not combine with hydrogen, but of which the valency may be determined with reference to univalent chlorine or bivalent oxygen. Take, for example, some of the compounds of potassium, calcium, bismuth, and tin:

$K^{i}Cl^{i}$. $Ca^{ii}Cl_2^{i}$. $Bi^{iii}Cl_3^{i}$. $Sn^{iv}Cl_4^{i}$.
$K_2^{i}O^{ii}$. $Ca^{ii}O^{ii}$. $Bi_2^{iii}O_3^{ii}$. $Sn^{iv}O_2^{ii}$.

In many cases valency may be made clearer to the eye by a different use of symbols. For instance, carbon unites with hydrogen and chlorine to form the following series of compounds:

$$C\left\{\begin{matrix}H\\H\\H\\H\end{matrix}\right. \quad C\left\{\begin{matrix}Cl\\H\\H\\H\end{matrix}\right. \quad C\left\{\begin{matrix}Cl\\Cl\\H\\H\end{matrix}\right. \quad C\left\{\begin{matrix}Cl\\Cl\\Cl\\H\end{matrix}\right. \quad C\left\{\begin{matrix}Cl\\Cl\\Cl\\Cl\end{matrix}\right.$$

Here we have the hydrogen-atoms successively replaced or *substituted* by chlorine-atoms, in such a way as to show at a glance the equivalency of these elements and the quadrivalency of the carbon.

Still another method of representing valency consists in attaching to the symbol of each element the necessary number of dashes, thus:

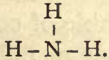
$$H-,\qquad O=,\qquad N\equiv,\qquad C\equiv,\ \text{etc.; or thus:}$$

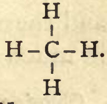
$$H-,\qquad -O-\qquad -\overset{|}{N}-\qquad -\underset{|}{\overset{|}{C}}-\ \text{etc.}$$

From these symbols we may derive a system of *structural* formulæ, as they are called, of which the following are good examples:

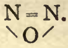
Free hydrogen, $H-H$, or H_2.
" oxygen, $O=O$, or O_2.
" nitrogen, $N\equiv N$, or N_2.

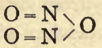
Water, $H-O-H$.

Ammonia,

$$\begin{array}{c} H\\ |\\ H-N-H \end{array}$$

Methane,

$$\begin{array}{c} H\\ |\\ H-C-H\\ |\\ H \end{array}$$

Carbon dioxide, $O=C=O$. Cyanogen, $N\equiv C-C\equiv N$.

Nitrogen monoxide,

$$\begin{array}{c} N=N\\ \diagdown O \diagup \end{array}$$

Nitrogen trioxide,

$$\begin{array}{l} O=N\diagdown\\ \qquad\quad O\\ O=N\diagup \end{array}$$
etc.

In some cases we encounter formulæ in which the conditions of valency are not satisfied. For instance, in nitrogen dioxide, NO, we have

$$-N=O,$$

and one of the valencies or *bonds of affinity* of the nitrogen-atom is uncombined. Such a compound is called an *unsaturated* compound, and it enters into further union with other elements with very great ease. Thus, from the compound just cited, by combination with chlorine, we get a substance having the formula $Cl-N=O$, and in which we see a triad united with a monad and a dyad in such a way that the valencies exactly balance. It will be seen at once that the molecules of free hydrogen, oxygen, and nitrogen are to be regarded as *saturated* compounds, while the free atoms, if they could exist separately, would be unsaturated. In many chemical changes the elementary atoms are probably set free, but immediately re-enter into union with each other to form molecules.

In the case of cyanogen we meet with a group of atoms which behaves like an element and is called a compound radicle. The formula of the gas is given above, and represents really two CN groups united to C_2N_2. The CN group itself, the true compound radicle, is univalent, thus:

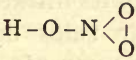
$$N\equiv C-$$

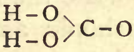
and therefore is capable of combining with elements in much the same way as chlorine. For example:

Chlorine, $Cl-Cl$.	Cyanogen, $CN-CN$.
Hydrochloric acid, $H-Cl$.	Hydrocyanic acid, $N\equiv C-H$.
Potassium chloride, $K-Cl$.	Potassium cyanide, $K-CN$, etc.

Care must be taken not to misapprehend the meaning of these "structural" formulæ. They are not intended to represent the relative position of the atoms in space, but merely to indicate to the eye the chemical relations of the substances thus symbolized. By their aid chemical reactions become more easily intelligible, and in many cases they help the chemist to predict the composition and best mode of preparing compounds even in advance of actual discovery. The whole theory of valency will become clearer when we study it in the light of organic chemistry; and one more illustration of it will suffice for the present chapter.

A brief reference was made in a previous chapter to three important classes of compounds, acids, bases, and salts. So far we have studied but two important acids—namely, nitric acid, HNO_3, and carbonic acid, H_2CO_3. These have the following structural formulæ:

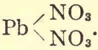
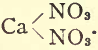




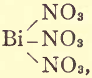
In these formulæ we may regard the NO_3 group of atoms, which is found in all nitrates, as univalent; while the CO_3 group, which characterizes the carbonates, is bivalent, as the two hydrogen-atoms united with it clearly show. Now, the salts of these acids are really formed by replacing the hydrogen by metals; and just here the laws of valency come into play. Thus, with univalent metals, nitrates are formed having formulæ like the subjoined:

$H-NO_3$. $K-NO_3$. $Na-NO_3$. $Ag-NO_3$.

With bivalent metals we get salts like these:

$Pb(NO_3)_2$, or  $Pb\begin{matrix}\diagup NO_3\\ \diagdown NO_3\end{matrix}$. $Ca(NO_3)_2$, or  $Ca\begin{matrix}\diagup NO_3\\ \diagdown NO_3\end{matrix}$.

And with a trivalent metal, like bismuth, we get—

$Bi(NO_3)_3$,   or  $Bi\begin{matrix}\diagup NO_3\\ -NO_3\\ \diagdown NO_3\end{matrix}$,   or BiN_3O_9.

Since these salts are called respectively potassium, sodium, silver, lead, calcium, and bismuth nitrates, it is plain that the acid itself might fairly be named hydrogen nitrate. That is, in acids, hydrogen, which is an essential constituent of every acid, behaves chemically like a metal, and gives us an additional argument in favor of its metallic character. These formulæ also show us that the nitrate of any metal may be represented as resulting from the combination of univalent NO_3 with the metal in a proportion depending upon the valency of the latter. Hence, if we know the valency of a metal, we can at once write the formula of its nitrate.

With carbonic acid similar rules hold good; only the hydrogen may be either partly or wholly replaced. Thus, we have:

H_2CO_3. $KHCO_3$. K_2CO_3. $NaHCO_3$. Na_2CO_3.
$PbCO_3$, $CaCO_3$, etc.

As we become acquainted with more acids, we shall find like principles always to be applicable; and that a knowledge of valency will enable us to write a vast number of formulæ which could not possibly be remembered unless connected by some such general law.

CHAPTER XIII.

THE CHLORINE GROUP.

THE four univalent elements, fluorine, chlorine, bromine, and iodine, are so similar in their chemical relations that they form an exceedingly definite natural group. In their differences they exhibit a remarkable gradation of properties, which follows the order of their atomic weights. In the free state fluorine is unknown, but chlorine is a greenish-yellow gas, bromine is a heavy, brownish-red liquid, and iodine is a black solid which forms beautiful purple vapors. With hydrogen, fluorine unites so strongly that the two elements can not be directly separated from each other; chlorine combines vigorously, bromine easily, and iodine only with difficulty. In general, chlorine acts more energetically upon other substances than bromine, while iodine is the least active of all. As a rule, the compounds of bromine have properties intermediate between those of chlorine and iodine. These three elements also resemble each other in odor.

FLUORINE is found in nature in various minerals, and minute quantities of its compounds also occur in bones, milk, and blood. Its atomic weight is 19, and its chief sources are the two minerals fluorspar and cryolite. The latter, which is brought in great quantities from Greenland, is a fluoride of aluminum and sodium, $3NaF,AlF_3$; and is used in making soda, alum, and porcelain glass. Just as the compounds of oxygen with other elements are called oxides, the compounds of fluorine are termed fluorides. So, also, we have chlorides, bromides, and iodides, formed by chlorine, bromine, and iodine respectively. With hydrogen these elements form acids, as follow:

Hydrogen fluoride, or hydrofluoric acid, HF.
" chloride, " hydrochloric " HCl.
" bromide, " hydrobromic " HBr.
" iodide, " hydriodic " HI.

So far, all attempts to isolate fluorine have been unsuccessful. Its chemical activity seems to be so great that the moment it is set free it combines at once with whatever substances may happen to be near it. It is also the only element which has not yet been made to combine with oxygen.

The only fluorine compound sufficiently important for description here is hydrofluoric acid. This is usually prepared by treating calcium fluoride, CaF_2, commonly known as fluor-spar, with sulphuric acid. Any other metallic fluoride would do, but this one is the most abundant. The reaction is as follows:

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF.$$

The pure acid is a very volatile liquid, having the most violently corrosive properties. A drop of it on the skin will produce a painful ulcer which may not heal for several weeks. Even the weaker acid containing water, such as is commonly prepared, has to be handled with extreme care.

Hydrofluoric acid is chiefly remarkable for its power of attacking glass, which may be shown by the following experiment:

EXPERIMENT 46.—Cover a sheet of glass with wax, and cut a design through the wax with the point of a needle. Make a small dish or tray out of a piece of sheet-lead, and in it mix some powdered fluor-spar to a paste with strong sulphuric acid. Place the prepared glass over this dish, face downward, and warm gently. Wherever the wax has been scratched away, the glass will be corroded.

This process is practically used for etching designs upon glass, for marking the graduation upon the stems of thermometers, and so on. The commercial acid contains much water, and is preserved in bottles made of gutta-percha.

CHLORINE, the atomic weight of which is 35.5, is by far the most important element of this group. It is found in nature in many compounds, the most abundant one being sodium chloride, $NaCl$, or common salt. This is the chemist's starting-point for the preparation of chlorine and of all its other compounds.

EXPERIMENT 47.—In a large flask provided with a delivery-tube mix one part of common salt, one of manganese dioxide, two of sulphuric acid, and two of water. Upon heating gently, chlorine gas will be evolved in a continuous stream, and may be collected by displacement (Fig. 28). It can not conveniently be collected over water or mercury, since it is quite soluble in the one and it corrodes the other.

In this experiment two different reactions take place. First, the sulphuric acid attacks the sodium chloride, forming sodium sulphate and setting hydrochloric acid free. The latter then reacts upon the manganese dioxide, giving up its hydrogen to unite with the oxygen of the latter, and so liberating the chlorine. The whole change is as follows:

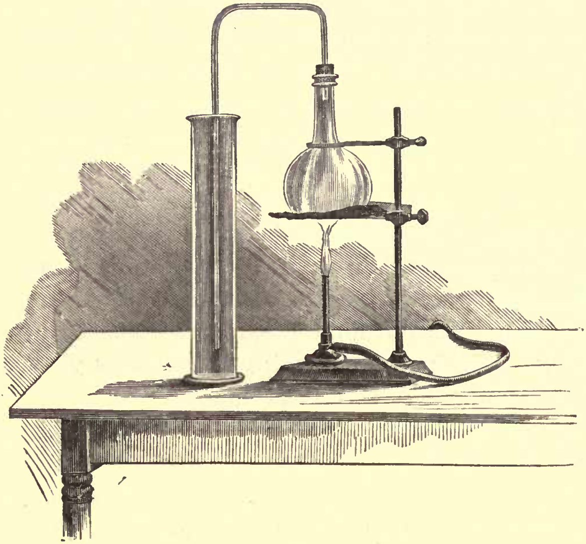


FIG. 28.—Preparation of Chlorine.

$$2NaCl + 2\ H_2SO_4 + MnO_2 = Cl_2 + Na_2SO_4 + MnSO_4 + 2H_2O.$$

A simpler but no better mode of preparation, involving the same apparatus, consists in treating the manganese dioxide directly with common hydrochloric acid. The reaction then is—

$$MnO_2 + 4\ HCl = MnCl_2 + Cl_2 + 2\ H_2O.$$

In either equation we have two atoms—that is, *one molecule*—of chlorine set free. There are still other processes for the manufacture of chlorine which are used on a large commercial scale, but they need no extended notice here.*

Chlorine was discovered by Scheele in 1774. It is a greenish-yellow gas, two and a half times heavier than air, and having a highly irritating odor. Even a trace of it, if inhaled, will produce a painful sense of suffocation. By cold and pressure it may be condensed to a heavy yellow liquid, but it has not yet been solidified.

Cold water absorbs about two and a half times its bulk of chlorine. The solution, which is known in the laboratory as chlorine-water, is yellowish, and smells strongly of the gas. It is a useful substance in some of the processes of chemical analysis, but it must be kept in the dark, or in a bottle covered with black paper. Exposed to the light, chlorine decomposes water, withdrawing hydrogen to form hydrochloric acid, and setting oxygen free.

EXPERIMENT 48.—Fill a small flask full of chlorine-water, prepared by passing chlorine into water as long as it dissolves, and invert it in a dish of the same solution. Leave the liquid for some time exposed to sunlight. Bubbles of oxygen will form, and collect in the upper part of the flask (Fig. 29), where they may easily be identified.

Chlorine unites vigorously with nearly all the elements, and especially with the metals. A bit of phosphorus, plunged into a jar of the gas, will spontaneously inflame; and powdered antimony or thin copper-foil will also ignite readily.

EXPERIMENT 49.—Prepare some chlorine by

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* A good outline of these processes is given in Wagner's "Chemical Technology."

either of the methods previously described, and dry it by allowing it to pass through a tube containing

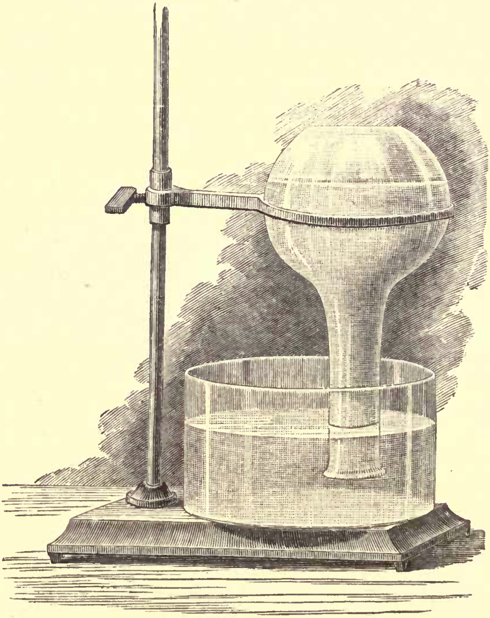

FIG. 29.—Formation of Oxygen from Chlorine-water.

lumps of calcium chloride. Into a jar of this perfectly dry gas throw some powdered antimony. The latter will burn brilliantly, filling the jar with dense fumes. Dip into another portion of the chlorine a piece of paper moistened with *warm* turpentine. This also will ignite and burn with a sooty flame. Into a third jar of the gas plunge a lighted candle. It will continue to burn with a reddish flame, emitting dense clouds of smoke. Combustion, then, although commonly due to oxidation, is not always so. It is simply a phenomenon of violent chemical action, and may be produced by union either with oxygen or other elements.

Although chlorine has a considerable number of uses in the arts, its chief practical importance is due to its property of bleaching vegetable colors. This is easily illustrated:

EXPERIMENT 50.—Dip some slips of litmus-paper, some bits of bright calico, and some highly-colored flowers into chlorine-water. They will be bleached. Add chlorine-water to a solution of indigo, and the latter will be decolorized. Characters written in ordinary ink may be obliterated by exposure to chlorine; but printer's ink, which consists of carbon, is not affected.

Chlorine is also a vigorous disinfectant. This property, and its value as a bleaching agent, both depend upon its strong affinity for hydrogen, which is partly illustrated in Experiment 48. The ignition of turpentine and the burning of a candle in chlorine are also due to the active union of this element with the hydrogen which they contain. In most cases chlorine is applied for bleaching or disinfecting purposes in presence of moisture. The latter gives up its hydrogen, and the oxygen thus set free acts with especial vigor, at the moment of its liberation, upon the coloring-matter or putrescent substance which is to be destroyed. Chlorine, therefore, may be regarded as indirectly an oxidizing agent; although in some cases it acts destructively upon obnoxious compounds by withdrawing hydrogen and so breaking up their molecules. These uses of chlorine will be considered further on, when we study the properties of bleaching-powder.

With hydrogen, chlorine forms but a single compound, hydrochloric acid, HCl; and some of the circumstances under which it is produced have been already described.

When equal volumes of hydrogen and chlorine are mixed together in the dark, they will remain without action upon each other for an indefinitely long time. If the jar or bottle containing them be exposed to ordinary diffused daylight, they will slowly and quietly combine; but if they are suddenly brought from darkness into the full glare of the sun, they will unite instantaneously with explosive violence. This may be experimentally verified by filling a flask in the dark with the gaseous mixture, wrapping it in a cloth, and then in strong sunlight pulling away the cloth by means of a long string. The flask will be shattered by the explosion which ensues. Light is frequently instrumental in bringing about chemical changes. In this case it produces chemical union; on the photographic plate it causes decomposition; and the fading of colored fabrics in sunlight also illustrates the same thing. Some of these matters will be further discussed in other connections.

EXPERIMENT 51.—An additional example of the direct union of hydrogen and chlorine is furnished by the combustion of the former gas in the latter. The apparatus may be arranged as in Fig. 30, hydrogen being generated in the flask in the usual way, while the jet dips into a cylinder or jar containing the chlorine. The hydrogen-flame should be first kindled in the air, with the ordinary precautions (see Experiment 7), and then lowered into the chlorine.

For practical purposes, however, hydrochloric acid is prepared by a wholly different method.

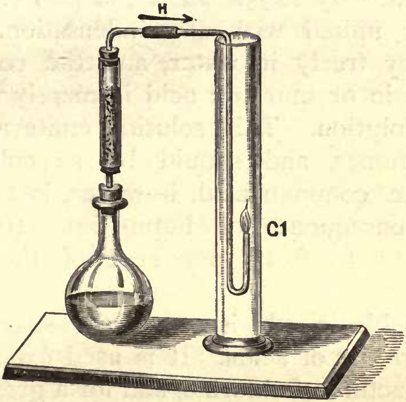

FIG. 30.—Combustion of H in Cl.

EXPERIMENT 52.—In a glass flask provided with a delivery-tube heat some perfectly dry common salt with about twice its weight of strong sulphuric acid. Hydrochloric acid will be evolved with much effervescence, and may be collected over mercury. If an aqueous solution of the gas is wanted, the delivery-tube may dip into a jar of water. As the experiment is conducted in the school-room, the reaction is as follows:

$$NaCl + H_2SO_4 = NaHSO_4 + HCl.$$

In making the acid on a commercial scale, a higher temperature is applied, and only half as much sulphuric acid is taken. The reaction then is:

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl.$$

When we study sulphuric acid and the sulphates, the full significance of these equations will appear.

Hydrochloric acid is a colorless gas of pungent odor, and density 18.75. In it the two component gases are united without condensation. It dissolves very freely in water, and the commercial hydrochloric or muriatic acid is merely its strong aqueous solution. This solution emits acrid, suffocating fumes, and should be as colorless as water; the common acid, however, is bright yellow, in consequence of impurities. It contains from thirty to forty per cent of the gaseous acid.

Hydrochloric acid is one of the strongest and most important of acids. It is used extensively in the manufacture of chlorine, and for a great variety of other purposes. It dissolves many of the metals, such as tin, zinc, and iron—hydrogen being evolved, and the chlorides of the metals being formed:

$$Zn + 2HCl = ZnCl_2 + H_2.$$
$$Fe + 2HCl = FeCl_2 + H_2.$$

In these reactions the metals replace the hydrogen of the acid, just as in the cases previously noticed; only the salts formed are chlorides. In a similar way hydrofluoric acid yields fluorides, hydrobromic acid yields bromides, and hydriodic acid yields iodides. The student may advantageously test the solvent properties of hydrochloric acid upon several of the commoner metals. Some will be dissolved, and others not attacked at all; and the solutions of the former may be made by evaporation to deposit crystals of chlorides.

Hydrochloric[*] and nitric acids mutually decompose each other, with evolution of chlorine:

$$HNO_3 + 3HCl = 2H_2O + NOCl + Cl_2.$$

The compound NOCl was referred to in a previous chapter. It is an orange-colored gas of slight importance. The mixture of acids is, however, very important; since, by virtue of the chlorine which it liberates, it has the power of dissolving gold. No single acid will do this; and so the alchemists gave the mixture the name of *aqua regia*, or royal water, gold being considered the king of metals. It also dissolves platinum.

EXPERIMENT 53.—In each of two test-tubes put a bit of gold-leaf. Cover one with nitric and the other with hydrochloric acid. Neither will be attacked. Mix the contents of both test-tubes, and warm gently. The gold will dissolve, forming a yellow solution.

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[*] When hydrochloric acid is spoken of, the aqueous solution is usually meant. The pure HCl is commonly specified as hydrochloric acid gas.

CHAPTER XIV.

THE CHLORINE GROUP—(*continued*).

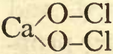
WITH oxygen chlorine does not combine directly; but, by indirect processes, three oxides, Cl_2O, Cl_2O_3, and Cl_2O_4, have been obtained. They are all gases of irritating odor and dangerously explosive character. With hydrogen and oxygen chlorine yields a remarkable series of acids, of which hydrochloric acid may fairly be considered the first member:

HCl,	Hydrochloric acid.
$HClO$,	Hypochlorous "
$HClO_2$,	Chlorous "
$HClO_3$,	Chloric "
$HClO_4$,	Perchloric "

It will be observed that chlorous and chloric acids resemble in formula nitrous and nitric acids, HNO_2 and HNO_3. The prefix *hypo*, which we meet in *hypo*chlorous acid, is often used to indicate compounds which are relatively low in a series. For example, *hypo*sulphurous and *hypo*phosphorous acids contain less oxygen than sulphurous and phosphorous acids respectively. The prefix *per*, on the other hand, as in *per*chloric acid, is expressive of higher combination. Thus we have the terms *per*oxide, *per*chloride, etc., applied to compounds more than ordinarily rich in oxygen or chlorine. These names are somewhat arbitrary, and no definite rule governs them without exception.

Hypochlorous acid, $HClO$, although unimportant by itself, forms some salts of the very highest importance. When chlorine gas is passed into a cold and dilute solution of caustic soda, it is copiously absorbed, and a mixture of sodium chloride and sodium hypochlorite, $NaClO$, is produced. The latter compound has a peculiar, sickish odor, and is used for disinfecting purposes. It forms the "Labarraque's solution" of the drug-stores. If chlorine be passed over slaked lime, instead of into caustic soda, a mixture of calcium chloride and calcium hypochlorite results from the action, and this is the well-known "chloride of lime," or bleaching-powder of commerce. The reaction which forms it is as follows:

$$2CaH_2O_2 + 2Cl_2 = 2H_2O + CaCl_2 + CaCl_2O_2.$$

The last symbol in this equation may be written  $Ca\begin{smallmatrix}\diagup O-Cl\\ \diagdown O-Cl\end{smallmatrix}$; and, when contrasted with H–O–Cl and Na–O–Cl, it serves to illustrate the bivalency of calcium.

Bleaching-powder is extensively used both for bleaching and as a disinfectant. It has the peculiar odor which is characteristic of all hypochlorites, and it owes its efficiency in great measure to the readiness with which it gives up its chlorine. In short, it affords us a convenient means of storing and transporting chlorine in an available form for most of its practical applications. At the beginning of this century all linen and cotton fabrics were bleached by long exposure on the grass to the action of sunlight and moisture. To-day they are bleached by chlorine, applied as a solution of calcium hypochlorite; and in a few hours, in a small area, more bleaching can be done than was formerly accomplished in several months on many acres of grass-land.

EXPERIMENT 54.—Shake up a quantity of "chloride of lime" with about four times its bulk of water; allow the mixture to settle thoroughly, and then carefully pour off the clear solution. With this solution repeat the bleaching experiments given under the heading of Experiment 50. In each case, however, first moisten the object to be bleached with very dilute sulphuric acid or with vinegar. Acids serve to liberate chlorine from bleaching-powder.

Chlorous acid and the chlorites are wholly unimportant; but in chloric acid and its salts we meet with compounds of considerable utility and interest.

EXPERIMENT 55.—Pass a stream of chlorine gas into a *weak* and *cold* solution of caustic potash. Potassium *hypochlorite*, K–O–Cl, will be formed, and may be recognized by its odor and bleaching properties. Now repeat the experiment with a *hot* and *strong* solution of the caustic potash. Potassium *chlorate* will be produced, and will be deposited in tabular crystals when the solution cools:

$$6KOH + 3Cl_2 = KClO_3 + 5KCl + 3H_2O.$$

Chloric acid itself has never been prepared quite free from water. In its most concentrated state it is a colorless, sirupy, intensely sour liquid, resembling nitric acid in many of its properties. It is so powerful an oxidizing agent that when it is merely dropped upon paper the latter will ignite.

The chlorates of potassium and sodium, $KClO_3$ and $NaClO_3$, are compounds of commercial importance. Potassium chlorate is especially useful as a source of oxygen in the manufacture of certain explosive mixtures, and as a medicinal agent. It is one of the favorite remedies for sore-throat. We have already met with it in Experiments 4 and 11, but the following experiments may also be profitably tried:

EXPERIMENT 56.—Allow a drop of strong sulphuric acid to fall upon a crystal of potassium chlorate. There will be violent action, and an evolution of yellow, pungent fumes. The latter consist of chlorine tetroxide, Cl_2O_4. If too much chlorate be used, an explosion may ensue; and if, as in Experiment 4, the salt be mixed with sugar or starch, the mass will take fire and burn brilliantly. A mixture of potassium chlorate with sugar forms a white gunpowder which, however, is too dangerous for practical use.

EXPERIMENT 57.—Put a bit of phosphorus as large as a pea at the bottom of a conical glass filled with water. A test-tube will answer, but is not quite so convenient. Throw in a few crystals of potassium chlorate, enough to cover the phosphorus, and then pour in a little strong sulphuric acid through a thistle-tube (Fig. 31). The phosphorus will presently catch fire, and burn vividly under water. The oxygen necessary for its combustion is, of course, supplied by the potassium chlorate. This experiment illustrates the ease with which chlorates give up their oxygen.

EXPERIMENT 58.—Rub vigorously together, in a porcelain or iron mortar, a pinch of potassium chlorate and a pinch of sulphur. Explosions more or less sharp will result from the friction. If a little of the mixture be placed on an anvil, or upon an iron plate, and struck with a hammer, the explosion will be almost deafening. Care, therefore, should be taken not to pulverize chlorates with other substances, although by themselves they may be rubbed to powder with safety. In this experiment we see that mechanical energy may produce a vigorous chemical action. All these experiments illustrate the peculiarities of chlorates in general, and not merely those of the potassium salt in particular.

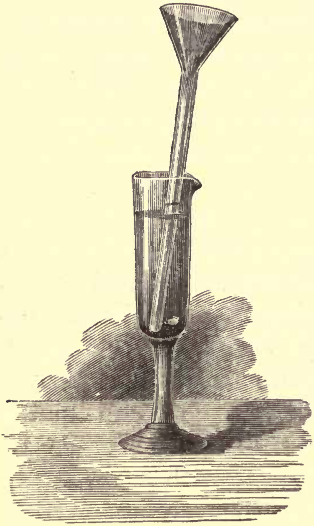


FIG. 31.—Combustion of Phosphorus under Water.

We have already learned that the most convenient mode of preparing oxygen is to heat potassium chlorate; the reaction being commonly written:

$$KClO_3 = KCl + O_3.$$

In reality, the reaction is much more complicated, and consists of two stages: First, part of the chlorate is decomposed by the heat, a portion of its oxygen being liberated, while the remainder goes to effect a further oxidation of some of the original salt. The equation is as follows:

$$2KClO_3 = KClO_4 + KCl + O_2.$$

In the second stage the $KClO_4$ is decomposed, thus:

$$KClO_4 = KCl + 2O_2.$$

The compound $KClO_4$ is potassium perchlorate; and from it, by proper means, perchloric acid, $HClO_4$, may be obtained as an oily liquid of specific gravity 1.782. Thrown upon paper or wood, the pure acid causes their immediate ignition; dropped upon charcoal, it explodes with terrific violence; in contact with the skin, it produces wounds which do not heal for months.

There is but one compound of chlorine with nitrogen, the formula being probably NCl_3. It is an oily liquid of such terribly explosive properties that it should never be prepared except by experienced chemists, and then only in very small quantities. It was discovered by Dulong, who lost an eye and three fingers in consequence of his discovery.

There are several compounds of carbon with chlorine; but as they are derivatives of hydrocarbons, they are usually described under the head of organic chemistry. A few formulæ will suffice for present examples:

CH_4 yields CCl_4.
C_2H_4 " C_2Cl_4.
C_3H_8 " C_3Cl_8.
C_6H_6 " C_6Cl_6.

Bromine, the third member of the chlorine group, is the only element known, except mercury, which is liquid at ordinary temperatures. It owes its name to a Greek word signifying a stench, because of its terribly suffocating odor. Its atomic weight is 80, its specific gravity in the liquid state is 3.187, and it boils at 63° centigrade. Its color is dark red, almost black; and it emits red fumes which somewhat resemble nitrogen tetroxide. It has some uses in analytical chemistry, and it is also employed in the manufacture of certain organic dyes. Some of the bromides, especially potassium bromide, are important medicinal agents; and they are also considerably used in the art of photography.

Bromine is chiefly found, as sodium or magnesium bromide, in sea-water and the waters of many mineral springs. At present it is produced in large quantities from some salt-wells in the Kanawha Valley of West Virginia. After the common salt has crystallized out from the brine, the remaining "mother liquor" is heated with manganese dioxide and sulphuric acid. These reagents liberate bromine in precisely the same way that they liberate chlorine; and the bromine is distilled off into a well-cooled receiver.

The compounds of bromine are strikingly similar to the compounds of chlorine, but are not quite so numerous. No oxide of bromine is known, but we have:

$HBrO_3$,	Bromic acid,
HBr,	Hydrobromic acid,
NBr_3,	Nitrogen bromide,
CBr_4,	Carbon tetrabromide, etc.

Salts are also known corresponding to hypobromous acid, $HBrO$ (a bleaching acid), and perbromic acid, $HBrO_4$.

IODINE is found in minute quantities in sea-water, from which, in the form of iodides, it is taken up by marine plants. It is obtained, commercially, from the ashes of sea-weeds, which are first treated with water. The solution thus obtained is then heated with manganese dioxide and sulphuric acid, and the iodine is thus set free. The reaction is precisely like that by which chlorine and bromine are prepared.

The element itself is a black solid with a metallic luster, and an odor faintly resembling that of chlorine. Its specific gravity is 4.95, and its atomic weight is 127. It is slightly volatile at ordinary temperatures, it melts at 115° C., and boils at 200°. Its vapor has a magnificent violet color; to which, from the Greek word meaning violet, it owes its name.

EXPERIMENT 59.—Put a fragment of iodine in the bottom of a dry test-tube, and heat gently over a flame. The violet vapors will recondense in the upper and cooler part of the tube. This process, by which a solid is vaporized and again condensed without passing through the intermediate liquid state, is called sublimation. The best commercial iodine is commonly labeled "resublimed."

EXPERIMENT 60.—Into the test-tube used for the last experiment, pour a little alcohol. The iodine will presently dissolve. The solution thus obtained is much used in medicine under the name of "tincture of iodine." Water will dissolve only a mere trace of the element.

EXPERIMENT 61.—Make a little starch-paste by warming common starch with water. A drop of tincture of iodine added to this will strike a deep-blue color. This is the ordinary test for free iodine.* Conversely, iodine is a test for starch.

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* Refer back to the test for ozone in the chapter on oxygen.

Experiment 62.—Mix a solution of potassium iodide with some of the starch-paste. Now add a few drops of chlorine-water. Iodine will be set free, and the mixture will become blue. Chlorine and bromine both liberate iodine from iodides.

Iodine and its compounds are much used in medicine, in photography, and in the preparation of certain aniline dyes. In general, the compounds resemble those of chlorine and bromine. Hydriodic acid, HI, is a colorless gas soluble in water. But one oxide is known—the pentoxide, I_2O_5, which is produced easily by the direct oxidation of iodine. There are also two acids, iodic and periodic, HIO_3 and HIO_4, which are much more stable than the corresponding compounds of chlorine.

With nitrogen iodine forms a compound which is curiously explosive. Its formula is probably NI_3, although it is rarely obtained perfectly pure.

Experiment 63.—Pour a little strong ammonia-water over some powdered iodine, and let it stand for half an hour. Filter the black sediment off upon several small filters, and spread these, while still wet, at a distance from each other to dry. When the powder, which is impure nitrogen iodide, is thoroughly dry, it will explode even at the touch of a feather. It is by far the most sensitive detonating substance known; and never more than a few grains of it should be prepared at a time.

The following table of formulæ may serve to assist the memory concerning the chief compounds of F, Cl, Br, and I:

HF	HCl	HBr	HI
———	$HClO$	$HBrO$	———
———	$HClO_2$	———	———
———	$HClO_3$	$HBrO_3$	HIO_3
———	$HClO_4$	$HBrO_4$	HIO_4
———	Cl_2O	———	———
———	Cl_2O_3	———	———
———	Cl_2O_4	———	———
———	———	———	I_2O_5
———	NCl_3	NBr_3	NI_3
———	CCl_4	CBr_4	CI_4

As we go on, we shall find that these elements always form closely similar compounds.

CHAPTER XV.

SULPHUR.

SULPHUR, selenium, and tellurium are three bivalent elements which, together with oxygen, form a second well-marked natural group. A few formulæ will show their chemical similarity :

H_2O	H_2S	H_2Se	H_2Te
H_2O_2	H_2S_2	———	———
CO_2	CS_2	———	———
OO_2 (ozone)	SO_2	SeO_2	TeO_2
———	SO_3	———	TeO_3
———	H_2SO_3	H_2SeO_3	H_2TeO_3
———	H_2SO_4	H_2SeO_4	H_2TeO_4

SULPHUR occurs abundantly in nature, both free and combined. Among the sulphides* we find the chief ores of lead, mercury, silver, copper, and antimony, and some of the commonest minerals containing iron and zinc. Calcium sulphate, or gypsum, exists in vast quantities, and other sulphates are frequently met with. Sulphur is also found in such animal substances as hair, albumen, etc., and in the pungent oils to which garlic, mustard, and horseradish owe their biting flavors. The blackening of

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* Formerly called sulphurets.

silver spoons by eggs is due to the formation of silver sulphide by the sulphur which the eggs contain.

Nearly all the sulphur of commerce is native sulphur from Southern Italy and Sicily. It is of volcanic origin, and occurs sometimes in brilliant crystals, but more commonly in opaque masses mixed with dirt. By a simple process it is melted out from its earthy impurities, after which it is refined by distillation, as shown in Fig. 32. The vapor passes from the retort into a large brick chamber, in which it condenses at once to the fine powder known as "flowers of sulphur." By degrees the walls of the chamber become heated, and then a

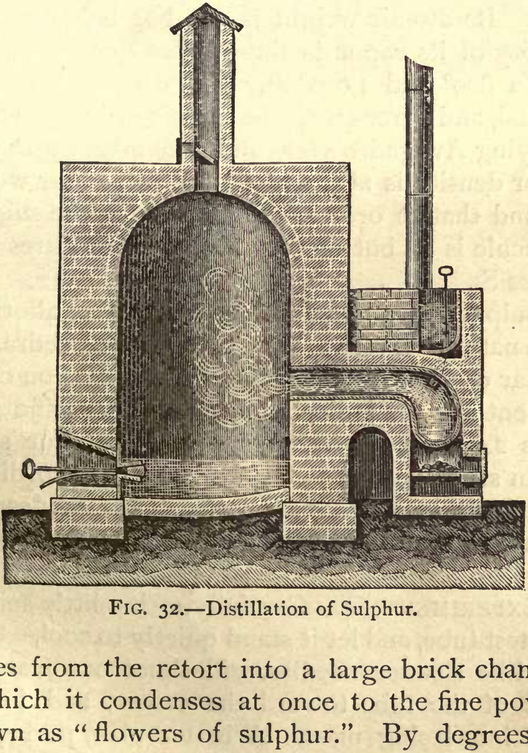

FIG. 32.—Distillation of Sulphur.

part, or even all, of the sulphur assumes the liquid state and is drawn off into molds. This gives the round sticks called "roll-brimstone." Still another variety of sulphur, "lac sulphur," is prepared by adding hydrochloric acid to a solution of calcium sulphide. It is precipitated as a fine white powder which is used in medicine.

Sulphur is ordinarily a yellow, brittle solid, without taste or odor. It dissolves in carbon disulphide, but not in water; it melts at 114.5° C., and boils at 448°. Its atomic weight is 32; but below 500° the density of its vapor is three times this, or 96. Between 800° and 1,000° the vapor density becomes normal, and agrees with the atomic weight. Hence, applying Avogadro's law, and remembering that the vapor density is always half the molecular weight, we find that at ordinary temperatures the sulphur-molecule is S_6, but at very high temperatures it becomes S_2.

Sulphur is a remarkable example of allotropy. The natural crystals are rhombic octahedra, and similar crystals are deposited from a solution of the element in carbon disulphide. Their specific gravity is 2.07. From fusion, however, sulphur solidifies in slender prisms of sp. gr. 1.98. Accordingly, sulphur is said to be *dimorphous*. A body capable of crystallizing in three distinct forms would be *trimorphous*.

EXPERIMENT 64.—Carefully melt a little sulphur in a test-tube, and let it stand quietly to cool, Crystals, like slender needles, will shoot out from the sides of the tube toward the center, and form a solid interlacing mass. A better plan, perhaps, is to melt a considerable quantity of sulphur in an earthen crucible, and let it cool until a crust forms over the top. Upon breaking this crust and pouring out the still fluid material beneath it, the crucible will be found to be lined with slender prismatic crystals. This is a general method for crystallizing substances from fusion. Bismuth, thus treated, yields superb crystals.

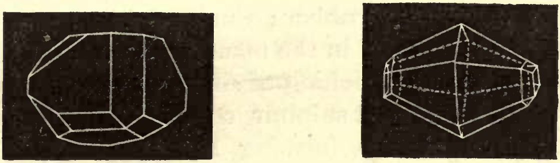

FIG. 33.—Crystals of Sulphur, both forms.

A third variety of sulphur, *plastic sulphur*, may be obtained by pouring melted sulphur into cold water.

EXPERIMENT 65.—Fill a test-tube half full of sulphur, and heat gradually over a flame. At 114.5° it will melt to a clear, amber-colored fluid, which, as the temperature rises, will become darker in tint and quite viscid. At 230° it will be almost black, and so thick that the test-tube may be inverted without a drop running out. Above 250° it again will become fluid, and if it be poured into cold water it will assume the form of a brownish mass which may be worked between the fingers like putty, or even drawn out into slightly elastic threads. By much kneading, or even by standing for a few days, the plastic mass will crumble and pass back into ordinary sulphur.

Sulphur combines easily with most of the other elements. In Experiment 1 its union with a metal was shown; and at this point the pupil may advantageously repeat the experiment with the three metals copper, iron, and zinc.* The element has many uses. It is an ingredient of gunpowder, of matches, and of vulcanized rubber; and immense quantities of it are consumed in the manufacture of sulphuric acid, and in the bleaching of silks and woolens.

With hydrogen, sulphur combines like oxygen in two proportions, forming H_2S and H_2S_2. The latter is an oily liquid, of nauseous odor and powerful bleaching properties, but having only theoretical importance.

Hydrosulphuric acid, also known as sulphhydric acid, or sulphuretted hydrogen, is a colorless gas having the peculiar odor of rotten eggs. Its density, as shown by the formula H_2S, is 17; and it burns with a blue flame to form sulphur dioxide and water: $H_2S + 3O = H_2O + SO_2$. In the concentrated state it is poisonous to inhale; and it may be reckoned as one of the more objectionable products of animal putrefaction. For laboratory purposes it is usually prepared by the action of dilute sulphuric acid upon iron sulphide, which latter substance is made by heating together iron-filings and sulphur.

EXPERIMENT 66. — Place some iron sulphide, broken into small fragments, in the flask previously used for the preparation of hydrogen, and pour over it some dilute sulphuric acid. The hydrosul-

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* A mixture of 32 parts of flowers of sulphur with 65 parts of zinc in the form known as "zinc-dust," may be ignited by a match. It burns with a beautiful greenish flame, leaving a bulky residue of yellowish-white zinc sulphide. In a confined space the combustion is explosive.

phuric acid will be given off with effervescence, and may be collected by displacement. Verify its combustibility as in the case of hydrogen, bearing in mind that it also makes an explosive mixture with air. By passing a stream of the gas through water a solution of it may be obtained, which will be of use in subsequent experiments. The present experiment may be represented by the subjoined equation:

$$FeS + H_2SO_4 = FeSO_4 + H_2S.$$

Hydrosulphuric acid is largely used as a test reagent in qualitative analysis, for the precipitation, as sulphides, of lead, copper, tin, antimony, bismuth, cadmium, etc.

EXPERIMENT 67.—Dissolve in water, in separate test-tubes or beaker-glasses, fragments of lead nitrate, copper sulphate, cadmium sulphate, and tartar emetic, and acidulate each solution with a few drops of hydrochloric acid. Now pass into each a few bubbles of H_2S, or add a little of the solution of the gas previously prepared, and note the character of the precipitates which form (Fig. 34). Solutions containing salts of other metals may also be tested. Some will yield precipitates and some will not; for example, if we have compounds of lead and iron dissolved together, we may throw down all the lead as solid lead sulphide, and filter it off, leaving the iron in solution. Thus the two metals can be easily and

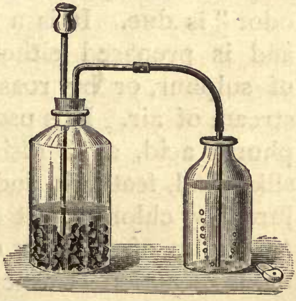

FIG. 34.—Precipitation by H_2S.

completely separated from each other. Two equations will illustrate the nature of these precipitations:

$$CuSO_4 + H_2S = CuS + H_2SO_4.$$
$$Pb(NO_3)_2 + H_2S = PbS + 2HNO_3.$$

EXPERIMENT 68.—Drop a solution of H_2S upon a bright silver coin or a bit of bright copper. A sulphide will be formed, the metal will be blackened, and hydrogen will be set free:

$$Cu + H_2S = CuS + H_2.$$
$$Ag_2 + H_2S = Ag_2S + H_2.$$

Sulphuretted hydrogen occurs in many mineral springs. The Blue Lick, White Sulphur, and Sharon waters all emit the gas copiously; and to it some of their medicinal value is ascribed.

Four oxides of sulphur are known—namely, SO_2, SO_3, S_2O_3, and S_2O_7. Only the first two are important. Sulphur dioxide, SO_2, is formed whenever sulphur burns, and to it the familiar "brimstone odor" is due. It is a colorless gas, of density 32, and is prepared either by the direct combustion of sulphur, or by roasting iron pyrites, FeS_2, in a stream of air. It is used in the manufacture of sulphuric acid, as a disinfectant, and for bleaching silk, wool, feathers, and straw, which would be injured by chlorine. It also serves to check the fermentation of wine or cider. As a disinfectant its mode of action is exactly opposite to that of chlorine. The latter in most cases oxidizes the bodies which are to be destroyed, while sulphur dioxide withdraws oxygen from them. As a bleaching agent, however, it seems to combine with the coloring-matter to form an unstable compound; and any substance which destroys the latter will bring the color back again. For laboratory purposes sulphur dioxide may be conveniently prepared as follows:

EXPERIMENT 69.—Heat some scraps of copper with strong sulphuric acid in the flask which was previously used for making chlorine. When a tolerably high temperature has been reached, sulphur dioxide will be freely evolved, according to the subjoined reaction:

$$Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O.$$

The gas may be collected over mercury, or by displacement. Instead of copper, charcoal may be used, but the sulphur dioxide produced will be impure.

EXPERIMENT 70.—Pass a stream of the gas from Experiment 69 into cold water. It will be absorbed, and with the solution, which will have the characteristic odor of SO_2, some bleaching experiments, like Experiments 50 and 54, may be tried. Sulphur dioxide bleaches only in presence of moisture.

The aqueous solution of sulphur dioxide may be formulated thus: $H_2O + SO_2 = H_2SO_3$. The latter symbol is that of sulphurous acid, which, like carbonic acid, unites with bases to form two sets of salts. For example, we have—

$$\begin{array}{ll} NaHSO_3 & KHSO_3 \\ Na_2SO_3 & K_2SO_3 \end{array}$$
$$CaSO_3, \text{ etc.}$$

The salts which retain half of their hydrogen are known as *acid* sulphites, or sometimes as *bi*sulphites. Those in which the replacement of hydrogen is complete are called *normal* or *neutral* salts. The sodium hydrogen sulphite, $NaHSO_3$, is sometimes used in paper-mills and chlorine bleacheries, to neutralize any excess of chlorine which might, if retained in the fabric, tend to weaken its fibers. Substances used for this purpose are termed " antichlors."

Sulphur trioxide, SO_3, may be prepared by the oxidation of SO_2 under peculiar circumstances, or by heating a compound known as pyrosulphuric acid, $H_2S_2O_7$. It usually forms long, silky, white needles, which unite with water, developing great heat, to generate sulphuric acid:

$$H_2O + SO_3 = H_2SO_4.$$

The similarity between this reaction and the one which yields sulphurous acid should be carefully noted. Although H_2SO_4 is one of the strongest acids known, SO_3 does not even redden litmus-paper. By some chemists these acid-forming oxides are termed *anhydrides*. Thus we have—

N_2O_5,	nitric	anhydride,	which	with	water	yields	HNO_3.
I_2O_5,	iodic	"	"	"	"	"	HIO_3.
CO_2,	carbonic	"	"	"	"	"	H_2CO_3.
SO_2,	sulphurous	"	"	"	"	"	H_2SO_3.
SO_3,	sulphuric	"	"	"	"	"	H_2SO_4.

CHAPTER XVI.

SULPHUR—(*continued*).

SULPHUR is remarkable for the number of acids which it forms by combination with hydrogen and oxygen. They are as follow:

1. H_2SO_2, Hyposulphurous acid.
2. H_2SO_3, Sulphurous "
3. H_2SO_4, Sulphuric "
4. $H_2S_2O_7$, Pyrosulphuric "
5. $H_2S_2O_3$, Thiosulphuric "
6. $H_2S_2O_6$, Dithionic "
7. $H_2S_3O_6$, Trithionic "
8. $H_2S_4O_6$, Tetrathionic "
9. $H_2S_5O_6$, Pentathionic * "

Most of these are unimportant, and need no further mention. Sulphurous acid has already been described; and thiosulphuric acid, which does not exist by itself, is of consequence only in one or two of its salts. Sodium thiosulphate, commercially known as "hyposulphite of soda," is very largely used in the art of photography. It serves to dissolve out from the photographic plate those compounds which have escaped the action of light, and which, if they were allowed to remain, would cause the photograph to fade.

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* The existence of this acid has lately been called in question.

In sulphuric acid, however, we find a compound which is undoubtedly the most important yet discovered by chemistry. It has so many and such varied uses that, as has been well said, the advancement of any nation in civilized arts may be measured by the amount of sulphuric acid which it consumes. Its annual production must be over a million tons;* and it is used in the manufacture of all the other strong acids, of chlorine, of soda, of alum, of phosphorus, of quinine, and of the more important fertilizers. It is also employed in refining fats and oils, in dyeing and bleaching, and as an exciting liquid in several forms of the galvanic battery. There is probably no great manufacturing industry which does not, directly or indirectly, make use of this acid. In nature it sometimes, though rarely, occurs uncombined. The waters of the Rio Vinagre, in South America, are rendered appreciably sour by its presence; and the Oak Orchard mineral spring at Medina, New York, contains nearly a gramme and a half to the litre. It is also found to a quite perceptible extent in the saliva of certain mollusks.

Commercially, sulphuric acid is prepared by oxidizing sulphurous acid with nitrous fumes. The process is essentially as follows:

Sulphur dioxide, generated by the combustion of sulphur, or by roasting iron pyrites in a suitable furnace, is passed into a large chamber, or series of chambers, lined with sheet-lead † (Fig. 35). Ni-

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* In Great Britain alone more than 850,000 tons are annually made.

† Such a chamber may be thirty metres long, six or seven wide, and five high; but the dimensions and arrangement are different in different places. An excellent account of the manufacture is given in Roscoe and Schorlemmer's "Treatise on Chemistry," vol. i, pp. 319–338.

trous fumes, produced by heating sodium nitrate with a little sulphuric acid, enter the chamber at the same time; jets of steam are blown in at several points, and a thorough draught of air is kept up throughout. The sulphur dioxide, meeting the nitric acid which enters the chamber with it, becomes oxidized into sulphuric acid, in accordance with the following reaction:

$$SO_2 + 2HNO_3 = H_2SO_4 + 2NO_2.$$

The NO_2, in presence of steam, oxidizes a fresh portion of sulphur dioxide, becoming itself reduced to NO; thus:

$$SO_2 + H_2O + NO_2 = H_2SO_4 + NO.$$

The last substance now takes up an atom of oxygen from the air, regenerating NO_2, but surrenders it at once to another portion of

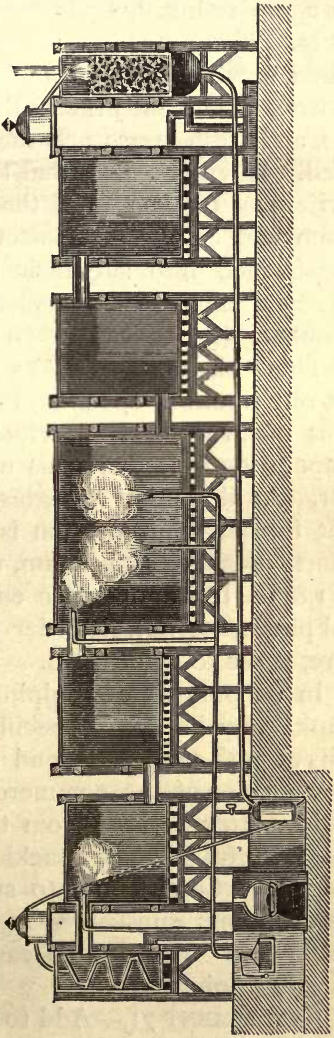


FIG. 35.—Sulphuric-Acid Manufacture.

the sulphurous acid; it is then reoxidized by more air, again reduced, again oxidized, and so on indefinitely. Theoretically a very small amount of NO_2 would serve to oxidize an infinite quantity of sulphurous acid; but practically there is always some loss, and fresh fumes are therefore constantly supplied. It will be seen that the fumes act simply as carriers of oxygen from the air to the mixture of steam and SO_2, which latter is being continually transformed into sulphuric acid by the process. The acid thus formed condenses on the floor of the chamber, whence it is drawn off.

This "chamber acid," as it is called, is a brownish, oily liquid of specific gravity 1.55. It still contains much water, from which it is partly freed by evaporation in leaden pans until its sp. gr. reaches 1.71. At this point it begins to attack the lead; so that further concentration is effected by heating in retorts of glass or platinum, until it attains a sp. gr. of 1.842. It is now pure enough for all commercial purposes; but, in order to render it *chemically* pure, it has to be distilled.

In its purest state sulphuric acid is a colorless, limpid, oily liquid, of specific gravity 1.854, which boils at 338° centigrade, and freezes at 10.5°. The brown color of the commercial acid is due to organic matter derived from the dust of the air. It is a powerful solvent, attacking many of the metals and converting them into sulphates, and charring such organic substances as wood, sugar, animal matter, etc. There is an easy experiment to illustrate this point.

Experiment 71.—Add to a very strong solution of white sugar in water, its own bulk of sulphuric acid. In a few moments it will blacken, swell up, and become a porous mass of charcoal. The explanation of this phenomenon is simple. Sugar contains carbon, hydrogen, and oxygen; the last two being present in just the proportions needful to form water. Sulphuric acid unites with water with intense avidity; accordingly, it withdraws the hydrogen and oxygen from the sugar, leaving the carbon behind. The corrosive action of sulphuric acid upon the skin and upon clothing is of the same general character as the foregoing.

The strong affinity of sulphuric acid for water is also indicated by the fact that when the two substances are mixed great heat is evolved. This may be verified by experiment in a test-tube or small beaker. The mixture, which often has to be made in the laboratory, should always be effected carefully; best by pouring the acid slowly into the water, and stirring the latter with a glass rod at the same time. By allowing gases to bubble through strong sulphuric acid, they may be thoroughly dried. For this purpose the arrangement shown in Fig. 36 is commonly employed. The gas-stream enters through the longer tube, which extends to the bottom of the flask, rises through the acid, and issues from the shorter tube. The ease with which sulphuric acid absorbs moisture from the air may be simply illustrated as follows:

EXPERIMENT 72.—Fill a test-tube one third full of strong sulphuric acid, and carefully mark its level on the side. Let it stand exposed to the air for a day or two, and again note the level of the liquid. The latter, by virtue of the absorbed water, will be found to have increased in bulk very perceptibly.

The affinity between sulphuric acid and water is really due to a distinct chemical action; for two definite compounds, called hydrates, are formed. Their formulæ are written thus:

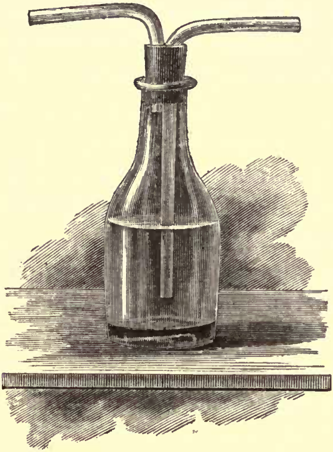


FIG. 36.—Washing-Flask for Gases.

$$H_2SO_4, H_2O,$$
$$H_2SO_4, 2H_2O.$$

At low temperatures these hydrates crystallize in characteristic forms.

Sulphuric acid was originally produced by a process quite distinct from that which is carried on in the leaden chambers. Sulphate of iron, or "vitriol," was distilled in earthen retorts, and an acid having the formula $H_2SO_4+SO_3$, or $H_2S_2O_7$, collected in the receivers. This was the "oil of vitriol" of the early chemists. It is now commonly known as "Nordhausen sulphuric acid," from the town in Saxony at which it is still made. It is also called "fuming sulphuric acid," from the fact that it emits white fumes of sulphur trioxide. The latter substance may be expelled by heating, when H_2SO_4 remains behind. By many chemists the compound $H_2S_2O_7$ is regarded as a distinct acid of sulphur, and to it the name of pyrosulphuric acid is applied.

Like sulphurous and carbonic acids, sulphuric acid is *dibasic*—that is, it contains two hydrogen-atoms which are replaceable by bases. Thus we have—

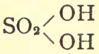
$KHSO_4$ $NaHSO_4$
K_2SO_4 Na_2SO_4
$CaSO_4$, etc.

The sulphates of sodium, calcium, magnesium, barium, iron, zinc, copper, etc., are all important compounds, which will be described in their proper connection further on.

In the ordinary process for making sulphuric acid, white crystals, called "lead-chamber crystals," are sometimes formed. Their formation, which occurs only when there is a deficiency of steam, may be illustrated on a small scale as follows:

EXPERIMENT 73.—Into a stoppered bottle, containing dry sulphur dioxide, introduce a glass rod moistened with nitric acid. Red fumes will appear, and after a short time white crystals will be deposited on the sides of the glass. Upon the addition of water they will dissolve with effervescence, giving off red fumes, and yielding sulphuric acid. Their formula is HSO_3NO_2, and they give us an important clew to the constitution or structure of the sulphuric-acid molecule.

In SO_2 we have a compound which may be regarded as a bivalent radicle. It unites with one atom of bivalent oxygen to form SO_3, and also with two atoms of univalent chlorine to produce sulphuryl chloride, SO_2Cl_2. With O and H_2O it yields sulphuric acid, which may be written structurally:

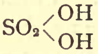


$$SO_2\begin{matrix}/OH\\ \backslash OH\end{matrix}$$

In this formula we meet with a peculiar group of atoms, which is essentially water minus half its hydrogen, and in all acid molecules this group occurs. It is called *hydroxyl*, and is necessarily univalent, since the oxygen in it is only half satisfied. Hydrogen dioxide, H_2O_2, is probably hydroxyl in the uncombined state; $(OH)_2$ being a molecule similar to H_2, Cl_2, and $(CN)_2$. Nitric acid, HNO_3, is structurally $OH{-}NO_2$, the NO_2 being another univalent radicle of great importance. Using these radicles, SO_2^{ii}, NO_2^{i}, and OH^{i}, we may now write the following structural formulæ:

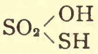
$SO_2{=}O$

Sulphur trioxide.



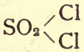
$$SO_2\begin{matrix}/OH\\ \backslash OH\end{matrix}$$

Sulphuric acid.



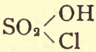
$$SO_2\begin{matrix}/OH\\ \backslash SH\end{matrix}$$

Thiosulphuric acid.



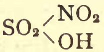
$$SO_2\begin{matrix}/Cl\\ \backslash Cl\end{matrix}$$

Sulphuryl chloride.



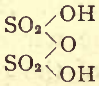
$$SO_2\begin{matrix}/OH\\ \backslash Cl\end{matrix}$$

Chlorosulphonic acid.



$$SO_2\begin{matrix}/NO_2\\ \backslash OH\end{matrix}$$

Lead-chamber crystals.



$$\begin{matrix}SO_2/OH\\ \quad >O\\ SO_2\backslash OH\end{matrix}$$

Pyrosulphuric acid.

Some of these compounds have only theoretical importance, and need not be specially described.

With nitrogen, chlorine, bromine, and iodine, sulphur forms various compounds; but only one of them, the chloride, S_2Cl_2, needs further mention here.

This substance is a volatile yellow liquid, produced by the direct union of its elements. It is somewhat used in a process for vulcanizing rubber.

With carbon, sulphur yields two compounds, CS and CS_2, analogous to CO and CO_2. The disulphide, CS_2, is produced by heating charcoal to redness in a stream of sulphur-vapor. It is a colorless, brilliant liquid of sp. gr. 1.29, which boils at 46°. Its odor suggests that of ether,* and its vapor forms an explosive mixture with air. It is very combustible, and burns according to the equation—

$$CS_2 + 6O = CO_2 + 2SO_2.$$

Its practical importance depends upon its solvent properties, it having the power of dissolving easily such substances as sulphur, phosphorus, rubber, fats, and oils. A solution of rubber in it gives a convenient water-proof varnish; and it is also used on the large scale for the extraction of fats from animal refuse. The number of its useful applications seems to be constantly increasing.

SELENIUM, atomic weight 79, is an element which is found as an occasional impurity of sulphur, and as a constituent of certain rare minerals. Its specific gravity varies from 4.25 to 4.80, and like sulphur it is allotropic. It has few uses, and these depend upon its remarkable electrical properties.

Seleniuretted hydrogen, H_2Se, is, like H_2S, a gas of intolerably nauseous odor. The dioxide, SeO_2, is a white solid which unites with water to form selenious acid, H_2SeO_3. Selenic acid, H_2SeO_4, is very similar to sulphuric acid, only not so strong. The

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* Commercial carbon disulphide has a nauseous odor, which is due to impurities.

selenates are *isomorphous* with the sulphates—that is, they crystallize in precisely the same forms.

TELLURIUM is another rare element having semi-metallic properties. It is tin-white, brittle, and has a sp. gr. of 6.25. It occurs in nature free, and also combined as tellurides with lead, bismuth, gold, silver, and mercury. The tellurides of gold and silver are important ores, especially in Colorado. The compounds of tellurium in general resemble those of selenium and sulphur. For example, H_2Te is a gas, and H_2TeO_3 and H_2TeO_4 are characteristic acids. No uses have yet been found for either the element or its compounds.

CHAPTER XVII.

PHOSPHORUS.

JUST as sulphur, selenium, and tellurium belong to the oxygen group of elements, so also phosphorus, arsenic, antimony, bismuth, and vanadium may be classed with nitrogen. Only two of these substances, however, phosphorus and arsenic, will be considered among the non-metallic elements.

Phosphorus exists in nature only in the combined state. It is found in many rocks, in all fertile soils, in plants, and in animals. Human bones contain more than half their weight of calcium phosphate, $Ca_3P_2O_8$; and in other combinations phosphorus is an important constituent of nervous matter and of the brain. Calcium phosphate is one of the commoner minerals, *apatite*, and is often found in large beds; and the phosphates of lead, iron, aluminum, manganese, copper, uranium, and magnesium form well-known mineral species.

The element itself was discovered by Brand of Hamburg, in 1669. It is now prepared on a large scale from bone-ash; or from sombrerite, an impure calcium phosphate found in West Indian guano. The powdered material, which is essentially $Ca_3P_2O_8$, is mixed with sulphuric acid and water, when calcium sulphate is formed and deposited as an insoluble white sediment. The remaining liquid, which is drawn off clear from this precipitate, contains an acid calcium phosphate, $CaHPO_4$, and is concentrated by evaporation to a thick sirup. This is mixed with powdered charcoal, thoroughly dried, and distilled in an earthen retort. Phosphorus is set free, vaporized, and recondensed under cold water. It is finally cast into sticks, and sent in this form into commerce.

As ordinarily seen, phosphorus is a yellowish-white, waxy solid, of specific gravity 1.837. It melts at 44.2°, and boils at 290°, giving a vapor of which the density is 62, or *double* the atomic weight. The molecule of phosphorus, therefore, is P_4. Phosphorus is highly inflammable, and on this account it is used in enormous quantities for the manufacture of friction matches. In handling it, care must be taken that it does not ignite in contact with the skin, for the burns which it produces are very painful, and troublesome to heal. It should never be cut except under water; and, indeed, it is always kept under water to protect it from oxidation. Exposed to the air at low temperatures, it oxidizes slowly, and the chemical action which thus takes place generates a feeble light. Hence, phosphorus becomes luminous in the dark; whence its name, which signifies "light-bearer." Whenever we rub a match over the palm of the hand in the dark, we recognize its luminous property. Although it is insoluble in water, phosphorus dissolves slightly in olive-oil and in ether, and freely in carbon disulphide. From its solution in the last-named liquid it may be obtained in crystals.

EXPERIMENT 74.—Dissolve a bit of phosphorus in CS_2, and pour the solution over a piece of unglazed paper. In a few moments the disulphide will evaporate, leaving the phosphorus spread over the paper in a very finely divided state. Under these circumstances it will ignite spontaneously, and the paper will burst into flame.

EXPERIMENT 75.—Cover a bit of phosphorus, no larger than a pea, with about a teaspoonful of finely powdered bone-black or lamp-black. The oxygen condensed by the carbon will presently cause the phosphorus to ignite.

When ordinary phosphorus is heated to 240° in an atmosphere free from oxygen, it becomes converted into an extraordinary allotropic form. This is a dark-red powder, which is opaque, insoluble in CS_2, non-luminous, and uninflammable. Its specific gravity is 2.11; and it may be dissolved in melted lead; from which, upon cooling, it will separate out in black crystals of metallic luster, and specific gravity 2.34. It is odorless, whereas common phosphorus has a faint odor resembling that of garlic; and it is not poisonous, although the other variety is a violent corrosive poison. Many rat and bug poisons are merely pastes containing ordinary phosphorus; and children have died in consequence of nibbling the tips off of common friction matches. By heating to 260°, red phosphorus may be retransformed into the common variety. Very recently another modification of phosphorus has been described by Remsen and Keiser. It is a white, flaky substance, produced by distilling common phosphorus in an atmosphere of hydrogen. In some respects it is analogous to flowers of sulphur, so that "flowers of phosphorus" would be a fair name for it. A black phosphorus has also been obtained by Thénard.

Although phosphorus forms three compounds with hydrogen, only one of them, PH_3, has any particular importance. This substance, phosphine, is a colorless gas, having a very disagreeable odor, and strongly resembling ammonia, NH_3, in its structure and chemical relations. Its formation is beautifully illustrated in the following experiment:

EXPERIMENT 76.—Arrange a small flask and delivery-tube, as in Fig. 37, and fill it nearly full of a solution of either caustic soda or caustic potash. Milk of lime, a mixture of lime and water, will do nearly as well. Add to the solution a few bits of phosphorus, and pour upon its surface a dozen drops of ether. The vapor of the latter merely serves as an aid in expelling from the flask the oxygen of the air. Upon boiling the solution, PH_3 will be evolved, and each bubble of the gas, on rising from the water of the water-pan, will ignite with a brilliant flash, and form a beautiful white ring of smoke. The absolutely pure gas is not spontane-

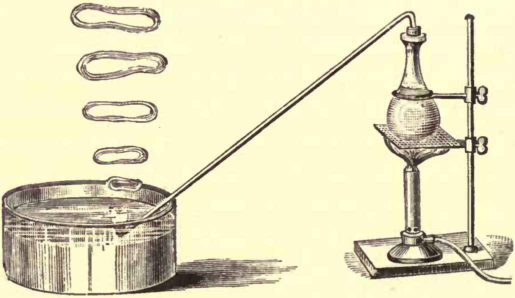


FIG. 37.—Preparation of PH_3.

ously inflammable; this property being really due to the presence, as an impurity, of traces of P_2H_4. Phosphine may also be formed by throwing calcium phosphide into water, when the same inflammable gas-bubbles will appear.

There are two oxides of phosphorus, P_2O_3 and P_2O_5, analogous to N_2O_3 and N_2O_5. The first is formed when phosphorus is oxidized slowly, the latter is the sole product of the combustion of the element. The one unites with water to form phosphorous acid, while from the other, under like circumstances, phosphoric acid is derived. The white smoke produced in Experiments 21 and 76 consisted of the pentoxide, which substance is chiefly remarkable for its intense affinity for water. It is by far the most powerful dehydrating agent known.

Phosphorus forms three distinct acids, as follow:

Hypophosphorous	acid,	H_3PO_2.
Phosphorous	"	H_3PO_3.
Phosphoric	"	H_3PO_4.

Salts corresponding to the first acid, hypophosphites, are produced by the action of alkalies upon phosphorus. One was formed in Experiment 76, and remained in solution. Several hypophosphites are used medicinally. Phosphorous acid and the phosphites are unimportant, except theoretically.

Phosphoric acid, the highest of the acids of phosphorus, is remarkable because of its existence in three distinct varieties having different formulæ. These may be represented simply as being formed by the union of P_2O_5 with one, two, and three molecules of water successively, as shown in the subjoined equations:

$P_2O_5 + H_2O = P_2H_2O_6 = 2HPO_3$, *meta*phosphoric acid.
$P_2O_5 + 2H_2O = P_2H_4O_7$, *pyro*phosphoric "
$P_2O_5 + 3H_2O = P_2H_6O_8 = 2H_3PO_4$, *ortho*phosphoric "

The salts of these acids are called *meta*phosphates, *pyro*phosphates, and *ortho*phosphates respectively, and they differ from each other in many particulars. Orthophosphoric acid is especially interesting as the first instance we have met with of a tribasic acid. Thus it forms three salts with sodium, as follows:

NaH_2PO_4.
Na_2HPO_4.
Na_3PO_4.

All the more common phosphates, such as calcium phosphate, $Ca_3^{ii}(PO_4)_2$, are orthophosphates. Such salts as $Ca^{ii}HPO_4$ and $KBa^{ii}PO_4$ are called *double* salts; and some triple phosphates also are known. For example, $NaAmHPO_4$, sodium ammonium hydrogen phosphate, is a *triple* salt. The last substance is much used in blow-pipe analysis under the name of microcosmic salt, or salt of phosphorus.

The compounds of phosphorus with the elements of the chlorine group have very great theoretical interest. Except in the case of the fluoride, they are formed by the direct union of the elements, and have the following formulæ:

		PF_5.
	PCl_3.	PCl_5.
	PBr_3.	PBr_5.
P_2I_4.	PI_3.	

There are also several oxychlorides, sulphochlorides, oxybromides, etc., having formulæ as follows:

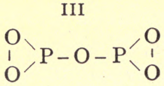
$POCl_3$. $POBr_3$. $PSCl^3$, etc.

Some of these bodies are very useful in the preparation of many organic compounds.

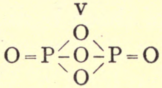
In the light of the foregoing formulæ we are at once led to ask a very serious question as to the valency of phosphorus. In PH_3 it is apparently trivalent, and also in PCl_3, PBr_3, and PI_3; but, in the higher compounds, PF_5, PCl_5, and PBr_5, it seems to have a valency of five. Which is the true valency, or are both equally correct?

A complete answer to this question would involve elaborate discussions entirely beyond the scope of this book. Suffice it to say that most chemists regard valency as a variable property of the elements, and that this variability is well illustrated by phosphorus, nitrogen, and sulphur. Hydrogen and carbon seldom, if ever, vary in valency, but the elements of the chlorine group seem to change occasionally. In NH_4Cl, N_2O_5, etc., nitrogen is regarded as quinquivalent; in SO_3, the valency of sulphur seems to be six; in Cl_2O_3 and I_2O_5, chlorine and iodine exhibit valencies of three and five respectively. In general, the elements may be divided into two great classes: one having valencies represented always by even numbers, as 2, 4, 6; the other running in odd numbers, as 1, 3, 5, etc. The even class are called *artiads*, the odd elements are called *perissads*. This division is, however, largely artificial, and represents no genuine law. To the rule there are several striking exceptions.

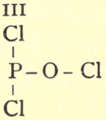
Some of the phosphorus compounds cited above may be assigned structural formulæ agreeing with a valency for the element of either three or five. For example, P_2O_5 may be written either



or

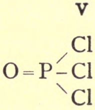


and $POCl_3$ may be represented by either



$$\overset{\text{III}}{\underset{Cl}{\overset{Cl}{P}}}-O-Cl$$

or



The aim of the chemist always is to select that formula from among the possible formulæ which shall best indicate the relations of each compound to the other compounds which may be derivable from it.* In many cases a careful consideration of structural formulæ has led to important discoveries.

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* The subject of variable valency is well discussed in Wurtz's "Atomic Theory," Remsen's "Theoretical Chemistry," and Cooke's "Chemical Philosophy."

CHAPTER XVIII.

ARSENIC, BORON, AND SILICON.

ARSENIC, which is sometimes classed as a metal, occurs in the mineral kingdom under a great variety of circumstances. The free element, its two sulphides, several arsenides, and a number of arsenates are common mineral species; but, for commercial purposes, it is chiefly obtained from arsenopyrite, a sulphide of arsenic and iron. This mineral, finely powdered, is heated in long earthen tubes; when arsenic, being volatile, sublimes, and is collected in the form of a brilliant, steel-gray, brittle, seemingly metallic mass.

Thus prepared, arsenic has a specific gravity of 5.7. There is also a black allotropic modification, of which the specific gravity is only 4.71. When heated under ordinary circumstances, it vaporizes without first melting; but, in a closed vessel, under pressure, it may be fused. The density of the vapor is 150, although the atomic weight of arsenic is only 75. Hence the molecule of the free element is As_4, and similar in structure to the molecule of phosphorus. The odor of the vapor resembles that of garlic; and its development before the blow-pipe flame gives us an easy means of detecting arsenic in minerals. A very impure arsenic is sometimes sold as a fly-poison, under the incorrect name of "cobalt"; but the only important use of the element is for hardening lead shot.

In their chemical relations the compounds of arsenic closely resemble those of phosphorus. They are also in many respects quite similar to the corresponding compounds of nitrogen. This is shown in the following formulæ:

NH_3	PH_3	AsH_3
N_2O_3	P_2O_3	As_2O_3
N_2O_5	P_2O_5	As_2O_5
HNO_3	HPO_3	———
———	H_3PO_4	H_3AsO_4
NCl_3	PCl_3	$AsCl_3$, etc.

Like phosphorus, arsenic has a valency of either three or five.

Arseniuretted hydrogen or arsine, AsH_3, is a colorless gas of terribly poisonous character. Its discoverer, Gehlen, accidentally inhaled a single bubble of the pure compound, and died in consequence. It is easily inflammable, depositing arsenic upon any cold substance which may be inserted in its flame; and this fact is always applied in the detection of arsenic.

EXPERIMENT 77.—Generate hydrogen as in Experiment 7; and, observing the necessary precautions, kindle the stream of gas issuing at the jet. Now pour into the generating-flask, through the thistle-tube, a few drops of a solution of any compound of arsenic. Hold a piece of cold porcelain against the flame, and a black, mirror-like stain of metallic arsenic will be deposited upon it. This stain will be volatile, and may be driven away by too much heat. Antimony compounds will give a similar reaction, owing to the formation of SbH_3; but the arsenic stain is soluble in a solution of sodium hypochlorite, whereas the antimony stain is not. This test is known as Marsh's test for arsenic.

There are two oxides of arsenic, As_2O_3 and As_2O_5. The first of these, arsenic trioxide, is the common white arsenic of commerce, well known on account of its poisonous properties. It is formed whenever arsenic is burned in the air; but it is usually manufactured on a large scale by roasting arsenopyrite, FeSAs. It is a white solid, which is volatile at about 220° C., giving a colorless and odorless vapor. It occurs in two different modifications—one crystalline, the other amorphous; the latter is the commercial form of the compound, and usually is found in lumps which curiously resemble porcelain. It is slightly soluble in water, forming probably arsenious acid, H_3AsO_3. From this acid, many arsenites are derived, and some of them have practical importance. Sodium arsenite is used as a mordant in calico-printing; and a double salt of copper arsenite and copper acetate is known commonly as Paris-green. This brilliant pigment is used extensively for coloring wall-papers, although the paper so tinted is certainly unwholesome. Whenever a sample of wall-paper is changed from green to blue by a drop of ammonia-water, or, when burned, gives a green tinge to the flame, the presence of an arsenic green may safely be inferred. The test is really a test for copper; but nearly all green pigments containing copper contain arsenic as well.* Paris-green is also used in enormous quantities for the destruction of the Colorado potato-beetle. Inasmuch as it is violently poisonous, it should be handled with extreme care. Arsenic trioxide itself is used in the preparation of the foregoing compounds, in glass-making, and in the manufacture of aniline red. When the last-named color is carelessly made, it is apt to retain injurious traces of arsenic. In cases of arsenical poisoning the best antidotes are freshly precipitated ferric hydroxide and caustic magnesia. These substances unite with arsenious acid to form insoluble arsenites, and thus prevent its absorption by the system. An emetic is subsequently used to remove the poison from the stomach.

Arsenic pentoxide, As_2O_5, is a white powder prepared by oxidizing the trioxide with nitric acid. It unites with water to form orthoarsenic acid, H_3AsO_4, which is strictly analogous to orthophosphoric acid, H_3PO_4, and yields similar salts. No acids of arsenic corresponding to pyrophosphoric and metaphosphoric acids have yet been obtained; but pyroarsenates and metarsenates, resembling the pyrophosphates and metaphosphates, are well known.

The fluoride, chloride, and bromide of arsenic, AsF_3, $AsCl_3$, and $AsBr_3$, are all volatile liquids; the iodide, AsI_3, is a solid compound. There are three sulphides of arsenic, As_2S_2, As_2S_3, and As_2S_5. The first is a brilliant red mineral, called realgar; and the second, which is also a natural mineral, is the

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* Brunswick-green, an oxychloride of copper, is the most important exception to this statement. When doubt arises as to the presence of arsenic, use Marsh's test for verification.

golden-yellow orpiment. Both were formerly much used as pigments. The trisulphide may be easily produced artificially by adding a little hydrochloric acid to a solution of the trioxide, and passing in a stream of sulphuretted hydrogen. It forms a brilliant yellow precipitate. The pentasulphide is also yellow, and is best known in combination with other sulphides. For example, corresponding to sodium arsenate, Na_3AsO_4, we have sodium sulpharsenate, Na_3AsS_4. The latter is related to arsenic pentasulphide in the same way that the former is related to arsenic pentoxide. Many similar double sulphides, called by the general name of sulpho-salts, are well known.

BORON, atomic weight 11, is a trivalent element which occurs as a constituent of many minerals. It is chiefly found, however, in boric (or boracic) acid, H_3BO_3, and borax, an acid borate of sodium. The element itself exists in two modifications; the one a dark-brown powder, the other a crystalline variety. In the latter form, which is never quite pure, boron has a specific gravity of 2.68, is infusible, and is nearly as hard as diamond. The crystals are square octahedra.

The compounds of boron are all formed upon a simple trivalent type; as, for example, the fluoride, BF_3, and the chloride, BCl_3. The former is a colorless gas, the latter is a volatile liquid. The hydride, BH_3, is also gaseous, and resembles NH_3, PH_3, and AsH_3 in structure. From boron trioxide, B_2O_3, by union with water, three acids are derived, as follows:

$$B_2O_3 + H_2O = 2HBO_2, \quad \text{metaboric acid.}$$
$$2B_2O_3 + H_2O = H_2B_4O_7, \quad \text{pyroboric “}$$
$$B_2O_3 + 3H_2O = 2H_3BO_3, \quad \text{orthoboric “}$$

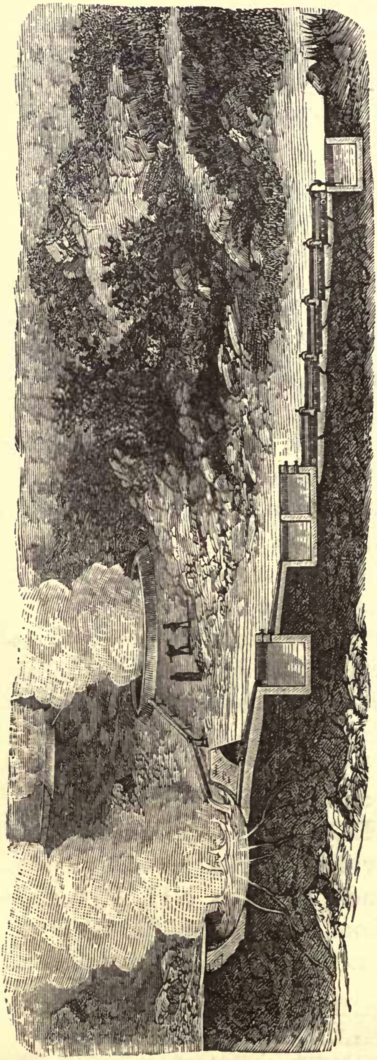

FIG. 38—Preparation of Boric Acid.

Orthoboric acid, $B(OH)_3$, is chiefly obtained from a volcanic region in Tuscany. Jets of steam, called *suffioni*, there issue from crevices in a mountain-side, bringing boric acid with them. A tank of masonry is built around each jet, and filled with cold spring-water. This condenses the boric acid, and then flows to a lower tank in which more acid is received, and so on down to the foot of the mountain (Fig. 38). At the bottom the water is evaporated in leaden pans, and the acid is deposited in white, shining, crystalline scales, which feel something like paraffin or spermaceti. It is used for the manufacture of borax, or sodium pyroborate, $Na_2B_4O_7 10H_2O$.

Borax is by far the most important compound of boron. It is not only made from boric acid, but it is also found in great quantities in the water of certain saline lagoons in Thibet, and in the Borax Lake of California. It has a feebly alkaline reaction, and is used to some extent in the household for laundry purposes, and for driving away water-bugs. Its important uses, however, are due to the power which it possesses of dissolving, when in the fused state, many metallic oxides. It serves as a flux in metallurgical operations, and for cleansing metallic surfaces which are to be brazed together. It is also very largely employed in making colored glazes and enamels for pottery and porcelain. Its use in this direction is indicated on a small scale by its applications to blow-pipe analysis. Make a small loop on the end of a platinum wire, and fuse in it enough borax to make a little, glassy bead. Add to this a trace of any manganese compound, and heat before the blow-pipe, and it will acquire an amethystine tinge; cobalt compounds will yield a blue color, chromium compounds an emerald-green, and so on. Each color gives a characteristic test for the metal whose compounds produce it.

The ten molecules of water contained in borax are called water of crystallization. Water so combined forms an essential part of very many crystallized salts, and is easily expelled by heating. When borax is fused it first melts in its own water of crystallization; and when the latter is wholly expelled, $Na_2B_4O_7$ remains behind. This anhydrous borax, on account of its glassy appearance, is often called "glass of borax." When a solution of borax is mixed with strong sulphuric acid, crystalline scales of boric acid are deposited upon cooling.

EXPERIMENT 78.—Dissolve a few crystals of borax in the least possible quantity of water, and add to the solution an equal bulk of strong sulphuric acid. Allow the mixture to cool, and note the formation of boric acid. Transfer the whole to a shallow porcelain or earthen dish, cover it with a layer of strong alcohol, and ignite. The alcohol will burn with a flame which is distinctly greenish, especially upon the edges. By the production of this green flame boric acid is easily detected analytically.

But one more non-metal remains to be considered; namely, SILICON.* This element, after oxygen, is the most important ingredient of the earth's crust, and enters largely into the composition of all the commoner rocks except dolomite and limestone. Granite, slate, clay, and sandstone are all compounds of silicon.

The element itself has an atomic weight of 28, and is, like carbon, quadrivalent. It is prepared by heating together metallic potassium and potassium silicofluoride, K_2SiF_6; and, like carbon, may be obtained in three different modifications. Of these, one is an amorphous, dark-brown powder; the second forms hexagonal plates resembling graphite; and the third crystallizes in octahedrons. It fuses at very high temperatures, and is insoluble in all acids except hydrofluoric. It has no practical importance.

The compounds of silicon are numerous and

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* Sometimes called silicium.

complicated. With hydrogen it forms a colorless, inflammable gas, SiH_4; with chlorine, bromine, and iodine it yields the compounds $SiCl_4$, $SiBr_4$, and SiI_4. The compounds $SiCl_3Br$, Si_2Cl_6, Si_2Br_6, and Si_2I_6 are also known. Silicon-chloroform, $SiHCl_3$, is interesting on account of its close similarity to ordinary chloroform, $CHCl_3$. There are several series of silicon compounds which resemble in chemical structure the organic compounds of carbon.

Silicon fluoride, SiF_4, is a colorless, corrosive gas which is produced whenever hydrofluoric acid acts upon other silicon compounds. The corrosion of glass by hydrofluoric acid is due to the formation of this fluoride. It is usually prepared by mixing powdered fluor-spar, CaF_2, with fine sand, and heating the mixture in a glass flask with strong sulphuric acid. If the gas is passed into water, a complex reaction ensues; a jelly-like mass of silicic acid is deposited, and a new acid, hydrofluosilicic acid, H_2SiF_6, remains in solution. This acid is much used as a test reagent in chemical analysis. From it, by replacement of hydrogen, a large series of salts may be derived.

It is in its oxygen compounds, however, that silicon is of the greatest importance. It forms one well-defined oxide, SiO_2, analogous to CO_2; and this oxide is not only found by itself in nature, but combined in a vast number of minerals. It also occurs in the vegetable kingdom, giving strength and stiffness to the stems of many plants. The shiny surfaces of grass-stems, of rattan, and of the scouring rush, are especially rich in silicon dioxide or silica.

In its purest form silica crystallizes in six-sided prisms, and is called quartz or rock-crystal (Fig. 39). The crystals are often very large and very limpid; and serve, when properly cut, for making spectacle-lenses, or as substitutes for the diamond. They are infusible, except before the oxyhydrogen blow-pipe, and are hard enough to scratch glass. Frequently quartz is colored by impurities, and then is known by a variety of special names, such as rose quartz, smoky quartz, etc. Yellow quartz is called false topaz; and the violet-colored variety is the well-known gem amethyst. Chalcedony, onyx, jasper, carnelian, agate, and flint, are merely varieties of quartz; sand and sandstone are the same substance, more or less impure. Perfectly white sand is nearly pure silica; the yellowish and reddish kinds owe their color to oxide of iron. Opal is an amorphous silica, containing a little water.

FIG. 39.—Group of Quartz Crystals.

Silicon dioxide is insoluble in water, and is attacked by no acid except hydrofluoric. Very strong and hot alkaline solutions dissolve it slightly, forming silicates; but the latter compounds are best prepared by fusing sand with sodium or potassium carbonate. If the sand is not in excess, the fused mass will dissolve in water, yielding a solution of the alkaline silicate. These silicates of sodium and potassium are known commonly under the name of water-glass, and have various uses. They serve to harden building-stones, and are used in making artificial stone; they are introduced into certain kinds of soap, and they are applied to mordanted calico previous to dyeing. They vary in composition; but in general a silicate may be compared with the corresponding carbonate, so that K_2SiO_3 is similar in structure to K_2CO_3. Most of the silicates, except those just mentioned, are insoluble; and the majority of those known occur as natural minerals. Feldspar, hornblende, mica, etc., are common examples; and garnet, emerald, topaz, and chrysolite are well-known gems. Granite, syenite, trap, and slate are mixtures of silicates, some of which are exceedingly complicated in their composition. The natural silicates are best described in the larger treatises on mineralogy.

Glass, porcelain, and pottery are artificial mixtures of silicates. Porcelain and pottery, in general terms, are more or less impure silicates of aluminum, and are infusible. Crown or window glass is a silicate of calcium and sodium; Bohemian glass is a silicate of calcium and potassium; flint or crystal glass is a silicate of potassium and lead. Green bottle-glass is like window-glass, except that it contains silicates of iron derived from the cheap and impure materials of which it is made. Other kinds of glass are also known, containing still other bases, but they are unimportant.*

If hydrochloric acid be added to a strong solution of water-glass, a jelly-like mass of silicic acid or silicic hydrate will separate out. To this mass the formula $Si(OH)_4$, which represents *ortho*-silicic acid, is usually assigned; but it rapidly loses water and becomes converted into *meta*-silicic acid, H_2SiO_3. If the solution of water-glass is sufficiently dilute, no separation of silicic acid will occur, but all will remain dissolved. Place such a solution in a vessel made by tying a piece of bladder or parchment-paper tightly over the bottom of a broad wooden hoop, and partially immerse the latter in a larger vessel of water for several days. The hydrochloric acid and the alkaline chloride will slowly diffuse through the bladder into the water, and in the hoop a clear, tasteless solution of silicic acid will remain. This, upon long standing, will solidify to a jelly. We have, then, two modifications of silicic acid—one soluble, the other insoluble—and the former is found in small quantities in many natural waters. The geysers of Iceland and of the Yellowstone Park contain it notably, and incrustations of silicon dioxide are deposited around their edges.

The process by which the foregoing solution of silicic acid was obtained is called *dialysis*. The hoop and membrane constitute a *dialyzer*. Through such a membrane crystallizable bodies, like salt, sugar, etc., diffuse easily, while non-crystallizable bodies,

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* The chemistry of glass and porcelain may be read up to advantage in Roscoe and Schorlemmer's "Treatise on Chemistry," vol. ii, part i, pp. 462–498; also in Wagner's "Chemical Technology," pp. 268–321.

like jellies, gum, glue, albumen, etc., can not pass at all. These two classes of bodies are termed, respectively, *crystalloids* and *colloids;* and when they occur in mixture they may be easily separated by dialysis.

CHAPTER XIX.

INTRODUCTORY TO THE METALS.

Of the seventy elements now known, fifteen have been described as non-metallic; the remaining fifty-two being reckoned as metals. Of these, some, like iron, copper, and lead, are familiar to everybody; while others, such as sodium and calcium, are somewhat outside of ordinary experience.

Between the metals and the non-metals no sharp line can be drawn. Neither group of elements can be rigidly defined, for they shade off gradually into each other. For example, arsenic and tellurium are sometimes called metallic, and at other times non-metallic; and with good reasons either way. The classification is merely one of convenience.

In general, however, the metals are distinguished by certain properties; one of the most noteworthy being the power of reflecting light in such a way as to produce the brilliant *metallic luster*. This is best seen on freshly-cut or scraped metallic surfaces before any film of rust or tarnish has had time to form. This property is shared by two or three non-metals, and by many compounds.

In color, nearly all the metals are whitish or grayish, like tin and silver. Calcium, strontium, and gold, which are yellow, and copper, which is dull red, are the only distinct exceptions. All are opaque, except occasionally in very thin layers. For example, gold-leaf transmits a little light of a greenish tinge.

Most of the metals are malleable and ductile; that is, they may be hammered into leaves and drawn into wire. Antimony and bismuth, however, are brittle, and may be pulverized in a mortar. In hardness they range from liquid mercury and soft lead up to iridium, which will scratch the hardest steel. In general, as compared with the non-metals, they are good conductors of heat and electricity.

In fusibility and specific gravity the metals differ widely. Mercury is liquid at all temperatures above −39·5° C., while platinum and some allied metals fuse only in the most intense heat of the electric arc or the oxyhydrogen blow-pipe. In lithium we have the lightest solid known, and in osmium the heaviest. The subjoined table of specific gravity and melting-point will be found useful for reference:

Melting-Point and Specific Gravity of some Metals.

NAME.	Melting-point.	Specific gravity.	NAME.	Melting-point.	Specific gravity.
Aluminum	850°	2.583	Columbium		7.06
Arsenic		5.727	Copper	1093°	8.945
Antimony	450°	6.700	Didymium		6.544
Barium		3.75	Gallium	30·15°	5.94
Bismuth	269	9.823	Glucinum		1.64
Cadmium	315°	8.67	Gold	1200°	19.298
Cæsium	26.5°	1.885	Indium	176°	7.421
Calcium		1.584	Iridium	1950°	22.421
Cerium		6.728	Iron	1800°	7.8
Chromium		7.3	Lanthanum		6.163
Cobalt	1800°	8.957	Lead	332°	11.335

NAME.	Melting-point.	Specific gravity.	NAME.	Melting-point.	Specific gravity.
Lithium	180°	0.585	Silver	1040°	10.512
Magnesium	750°	1.75	Sodium	95.6°	0.974
Manganese	1900°	8.013	Strontium		2.58
Mercury	39.44°	13.596	Tantalum		10.78
Molybdenum		8.60	Tellurium	400°	6.25
Nickel	1600°	8.900	Thallium	290°	11.91
Osmium		22.477	Thorium		11.23
Palladium	1500°	12.0	Tin	235°	7.3
Platinum	1779°	21.504	Tungsten		19.261
Potassium	62.5°	0.875	Uranium		18.685
Rhodium		12.1	Vanadium		5.5
Rubidium	38.5°	1.52	Zinc	423°	7.18
Ruthenium		12.261	Zirconium		4.15

The more important differences between the metals and the non-metals, however, are not physical, but chemical. In general terms the oxides of the non-metals unite with water to form acids, while those of the metals produce bases. The only acid-forming metallic oxides are those which contain unusually large proportions of oxygen. In order to make this matter clear, we must briefly consider the subject of electro-chemistry.

Whenever a current of electricity is passed through a compound liquid, the latter will be decomposed into two parts. In Experiment 19, water was so decomposed into oxygen and hydrogen, which were collected in separate tubes placed over the "poles," "terminals," or "electrodes," of the galvanic battery. This method of decomposition is called *electrolysis*, and the liquid which is analyzed is known as the *electrolyte*.

In the battery itself, with which we effect electrolysis, chemical action is taking place. In its simplest form the galvanic battery consists of a plate of zinc and a plate of copper immersed in dilute sulphuric acid, which acts unequally upon the two metals. Whenever we have such an inequality of action between two conductors in a conducting liquid, an electrical difference is produced which may be utilized as an electric current. The greater the inequality of action the stronger the current will be. In all cases the plate which is most attacked will be electro-positive; the other becoming at the same time electro-negative.* In the forms of battery most generally in use, zinc is the electro-positive element; the material of the other plate being varied. It would be possible, however, to use with zinc a metal which should be more vigorously attacked by sulphuric acid, and in that case the zinc would become electro-negative. When the terminal wires of a cell or battery are connected, the current flows *from* the positive element through the exciting liquid *to* the negative element, and then through the wires back to the positive plate to complete the circuit.

Now, when electrolysis takes place, as in the decomposition of water, we have the two terminal wires of the battery dipping separately into the liquid. The latter is separated by the current into two parts, one of which goes to one pole of the battery, and the other to the other pole. The part which appears at the pole connected with the zinc plate, is electro-positive; the part which appears at the other pole is electro-negative. In short, all the products of electrolysis exhibit electrical polarity;

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* For the full definition of these terms, as well as for the description of the different forms of battery, a work on physics must be consulted.

so that one becomes positive with respect to the other. Oxygen is electro-negative, hydrogen is electro-positive; between the two there is a strong chemical affinity. Between two electro-negative or two electro-positive elements, affinity is weak. Chemical affinity, then, bears a strong resemblance to electrical and magnetic attractions.

If, now, we subject a great many compounds to electrolysis, and note carefully at which electrodes the products of decomposition appear, we shall be able to arrange all the elements in an *electro-chemical series*, as follows. For present purposes we may ignore the rarer elements and confine our attention to the commoner substances:

Electro-negative.

Oxygen.
Sulphur.
Nitrogen.
Fluorine.
Chlorine.
Bromine.
Iodine.
Phosphorus.
Arsenic.
Chromium.
Boron.
Carbon.
Antimony.
Silicon.
Hydrogen.
Gold.
Platinum.
Mercury.
Silver.
Copper.
Bismuth.
Tin.
Lead.
Cobalt.
Nickel.
Iron.
Zinc.
Manganese.
Aluminum.
Magnesium.
Calcium.
Strontium.
Barium.
Lithium.
Sodium.
Potassium.

Electro-positive.

In this series, which should be read as if it were written in a *single* vertical column, each element is negative to those which follow it, and positive to those which precede it. Iodine, for instance, is the negative element in potassium iodide, but positive in its oxygen compounds. In general, however, *the non-metallic elements are strongly electro-negative,* *while the metals form the positive end of the chain.* Here we find the most essential difference between the two classes of elements. It must never be forgotten that "positive" and "negative," as here used, are only terms of comparison, and have no final significance. An element is positive under certain conditions, and negative under others, just as a hill is said to be low when compared with a mountain, and high when contrasted with a valley.

Electrolysis may be effected upon liquids under very varying circumstances. The liquid may exist at ordinary temperatures as a single, definite compound; it may be a substance kept in a state of fusion at a high heat; or it may consist of a salt dissolved in some fluid like water. In the latter case the chemical reactions may become quite complicated, as the following experiment and its explanation will show:

EXPERIMENT 79.—Fill a U-tube (Fig. 40) with a strong solution of sodium sulphate, colored with an infusion of red cabbage. Into the solution, at the two limbs of the tube, dip the terminals of a small galvanic battery, and allow the current to pass.

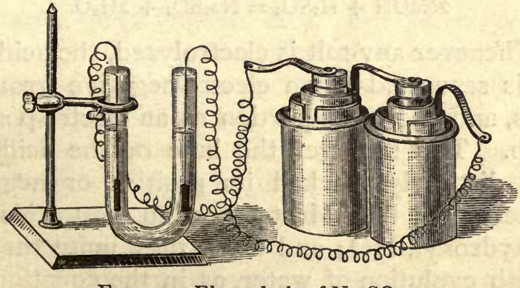

FIG. 40.—Electrolysis of Na_2SO_4.

At the pole which is connected with the zinc of the battery, the liquid will become alkaline, and turn green; at the other pole free acid may be detected, and the color remains red. By electrolysis, then, a neutral salt dissolved in water may be decomposed into an electro-negative acid and an electro-positive base. In the case under consideration, the reactions are as follows:

First, the Na_2SO_4 is split up into Na_2 and SO_4. The latter loses an atom of oxygen, which is given off at the proper pole, leaving SO_3. This unites at once with water to form H_2SO_4. At the other side of the equation the Na_2 decomposes some of the water, evolving hydrogen, and forming sodium hydroxide, NaOH, thus:

$$Na_2 + 2H_2O = H_2 + 2NaOH.$$

The latter compound is a strong alkali, and readily reunites with sulphuric acid, as follows:

$$2NaOH + H_2SO_4 = Na_2SO_4 + 2H_2O.$$

Whenever any salt is electrolyzed, the acid portion is separated as an electro-negative group of atoms, and the basic portion as an electro-positive group. The stronger the base or the acid, the more distinctly marked its positive or negative character will be. Most bases and most acids contain hydroxyl, HO; and when they unite they do so with evolution of water, as in the equation last given above. In forming a neutral salt, all of the hydrogen contained in the hydroxyl of both acid and base is thus removed. An acid salt retains part of the hydrogen of the acid; a basic salt retains some oxygen from the hydroxyl of the base.

In future chapters the applications of electrolysis to electrotyping and electroplating will be duly described.*

The metals, like the non-metals, are best classified according to valency. Thus, sodium and potassium are univalent, calcium and magnesium are bivalent, gold is trivalent, and tin is quadrivalent. The classification is most instructive, however, when we consider all the elements together, and ignore our old division into a metallic and a non-metallic group. Let us begin by arranging some of the elements in the order of their atomic weights, starting with hydrogen, the lowest:

H = 1.						
Li = 7.	Gl = 9.	B = 11.	C = 12.	N = 14.	O = 16.	F = 19.
Na = 23.	Mg = 24.	Al = 27.	Si = 28.	P = 31.	S = 32.	Cl = 35.5.
K = 39.	Ca = 40.	Sc = 44.	Ti = 48.	V = 51.5.	Cr = 52.	Mn = 55.

If, now, we consider any horizontal line in this table, we shall see that it begins with a univalent element; the next is bivalent, the third trivalent, the fourth quadrivalent, etc. Furthermore, the elements which are closely related to each other fall into the same vertical column, as Na and K, C and Si, N and P, O and S, F and Cl. Toward the left-hand side of the table the elements are strongly basic; toward the right they are distinctly acid-forming; in the middle columns the electro-chemical character is less definitely marked. If we study the chief oxides formed by these elements, some of the regularities due to valency will become very clear:

Na_2O.	Mg_2O_2.	Al_2O_3.	Si_2O_4.	P_2O_5.	S_2O_6.	Cl_2O_7.
K_2O.	Ca_2O_2.	Sc_2O_3.	Ti_2O_4.	V_2O_5.	Cr_2O_6.	Mn_2O_7.

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* Gore's work, "The Art of Electro-Metallurgy," is a most excellent little treatise upon this theme.

Here the proportion of oxygen steadily increases from one end of each line to the other. Six of the formulæ have been doubled in order to make this *ratio*, which is only a *ratio*, more apparent.

We see, then, that the elements vary in their chemical relations with a remarkable regularity, and that they seem to be connected with each other by some definite law. Were it not so, a bivalent element might be followed by one which was quadrivalent, and its next neighbor in turn might have any valency whatever. If we study the physical properties of the elements, similar regularities will confront us, at every step, of the most unmistakable character. In brief, it is now generally believed by chemists, although not as yet fully proved, that all the properties of an element depend in some way upon its atomic weight. For example, the specific heat of an element is inversely proportional to its atomic weight; or, in other words, all the elementary atoms have precisely the same capacity for heat. This point will be brought out more fully in another chapter.

On the opposite page a table of the elements is given, based upon the principles developed in the preceding paragraphs. This table is due chiefly to a Russian chemist, D. Mendelejeff,* who was able by means of it to predict the existence of two new elements long before they were actually discovered; namely, gallium and scandium. Wherever a blank occurs in the table, some element yet to be discovered probably belongs. Such blanks existed where gallium and scandium are now placed;

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* Similar tables were independently devised by Newlands and Lothar Meyer.

TABLE TO ILLUSTRATE THE CLASSIFICATION OF THE ELEMENTS.

SERIES	I. Valency 1.	II. Valency 2.	III. Valency 3.	IV. Valency 4.	V. Valency 3–5.	VI. Valency 2–6.	VII. Valency 1–7.	VIII. Valency 2–8.
1	H = 1.							
2	Li = 7.	Gl = 9.	B = 11.	C = 12.	N = 14.	O = 16.	F = 19.	
3	Na = 23.	Mg = 24.	Al = 27.	Si = 28.	P = 31.	S = 32.	Cl = 35.5.	
4	K = 39.	Ca = 40.	Sc = 44.	Ti = 48.	V = 51.	Cr = 52.	Mn = 55.	Fe = 56. Ni = 58. Co = 59. Cu = 63.3.
5	(Cu = 63.3).	Zn = 65.	Ga = 69.	———	As = 75.	Se = 79.	Br = 80.	
6	Rb = 85.5.	Sr = 87.5.	Yt = 89.	Zr = 90.	Cb = 94.	Mo = 96.	Ru = (?)	Rh = 104. Pd = 106. Ag = 108.
7	(Ag = 108).	Cd = 112.	In = 113.5.	Sn = 118.	Sb = 120.	Te = 126.	I = 127.	
8	Cs = 133.	Ba = 137.	La = 138.	Ce = 141.	Di = 145.	———	———	— — —
9	———	———	———	———	———	———	———	
10	———	———	Er = 166.	Yb = 173	Ta = 182.	W = 184.	Os = (?)	Ir = 193. Pt = 195. Au = 196.5.
11	(Au = 196.5)	Hg = 200.	Tl = 204.	Pb = 207.	Bi = 208.	———	———	
12	———	———	———	Th = 232.	———	U = 239.	———	— — —
	Oxide R_2O.	Oxide RO.	Oxide R_2O_3.	Oxide RO_2. Hydride RH_4.	Oxide R_2O_5. Hydride RH_3.	Oxide RO_3. Hydride RH_2.	Oxide R_2O_7. Hydride RH.	

The exact position of some of the rarer metals is still in doubt.

and from their position Mendelejeff foretold not only their existence, but also their leading properties. These predictions are now regarded as among the most remarkable achievements of modern science.* Unfortunately, the subject is not suited to thorough treatment in an elementary text-book.

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* For fuller discussions of Mendelejeff's "Periodic Law," the student may consult Roscoe and Schorlemmer's treatise, vol. ii, part ii, p. 506; or Wurtz's "Atomic Theory," p. 154.

CHAPTER XX.

THE METALS OF THE ALKALIES.

THE metals of the alkalies are five in number, and form a very definite univalent group. They exhibit a regular gradation in properties, which is well indicated in the following table :

NAME.		Atomic weight.	Specific gravity.	Melting-point.
Lithium,	Li..................	7.	0.585	180.°
Sodium,	Na (Natrium).......	23.	0.974	95.6°
Potassium,	K (Kalium).........	39.	0.875	62.5°
Rubidium,	Rb.............	85.5	1.52	38.5°
Cæsium,	Cs	133.	1.885	26.5°

All of these metals are silver-white, and soft enough to be easily cut with a knife. They are all readily oxidizable—so much so, that they have to be kept under naphtha to preserve them from the action of the air. Thrown upon water, they decompose it, forming soluble hydroxides and setting hydrogen free. This is done quietly by lithium, very violently by cæsium ; the other metals of the group being graded between these extremes.

EXPERIMENT 80.—Throw into a vessel of cold water a bit of potassium half as large as a pea. It will fuse, move about rapidly on the surface of the water, and seemingly burst into violet-colored flame. The flame is really due to the burning of the hydrogen which has been liberated. The color is caused by the vapor of the potassium. Sodium, under similar circumstances, will act in much the same way, only the action is not violent enough for the hydrogen to ignite. Thrown on wet paper, however, so that the heat of action may be confined to one spot, the hydrogen set free by the sodium will kindle, and burn with a yellow flame. The yellow color is characteristic of sodium and its compounds.

Concerning LITHIUM, RUBIDIUM, and CÆSIUM, little need be said. All three are comparatively rare. Lithium compounds are somewhat used in medicine, and give a magnificent red color to a flame. Rubidium and cæsium resemble potassium so closely that they are difficult to distinguish from it. They were discovered by spectrum analysis, which will be described in another chapter. The best source of the three metals is the rare mineral lepidolite. Cæsium is the most electro-positive element known. Hence it has a very strong affinity for electro-negative oxygen.

Before the introduction of systematic names into chemistry, soda, potash, and ammonia were known as mineral alkali, vegetable alkali, and volatile alkali, respectively. In 1807 Davy succeeded in decomposing soda and potash by means of a powerful electric current, and in isolating the metals which they contained. Soon afterward, chemical methods of preparing sodium and potassium were devised, the best one consisting in heating the carbonates of the metals with charcoal in an iron retort. The reaction which takes place is as follows:

$$Na_2CO_3 + 2C = Na_2 + 3CO.$$
$$K_2CO_3 + 2C = K_2 + 3CO.$$

The beak of the retort dips under naphtha—in which the vapor of the sodium or potassium, as it distills over, is condensed. Both metals are easily volatilized. As metals they have but few uses, although their compounds are of the highest practical importance. Sodium is used to some extent in the preparation of aluminum and magnesium, and is also of value in some lines of chemical research.

SODIUM is one of the most abundant of elements. The chloride exists in enormous quantities in sea-water, in many salt-lakes and mineral springs, as rock-salt, in marine plants, and in the various animal juices. The nitrate, the carbonate, and the borate occur in large natural deposits; cryolite, a fluoride of sodium and aluminum, forms an inexhaustible bed in Greenland; many silicates contain sodium as an essential ingredient.

The chief commercial source of sodium compounds is sodium chloride, NaCl, or common salt. Great beds of rock-salt, which is often perfectly transparent, are worked at Northwich in England, Wieliczka in Poland, Stassfurt in Germany, and the Island of Petit Anse in Louisiana. Near Syracuse, New York, Saginaw, Michigan, and in the Kanawha Valley of West Virginia, salt is made in vast quantities by the evaporation of natural brines which rise through artesian wells from subterranean springs. It is also prepared in many places from sea-water.

Sodium chloride crystallizes in cubes, and has a specific gravity of 2.15. As common salt, and in its use as a food-preservative and condiment, it is familiar to every one. It is also used in great quantities for the manufacture of chlorine and hydrochloric acid, as a fertilizer, and in the glazing of earthenware.

Sodium forms two oxides, Na_2O and Na_2O_2, but neither is important. The hydroxide, $NaOH$, however, is of great importance. When sodium is thrown into water, this substance, which is commonly called caustic soda, remains in solution; but practically it is usually prepared from the carbonate. The latter is dissolved in water and mixed with milk of lime; calcium carbonate is deposited as an insoluble white powder, and caustic soda remains in solution. By boiling down in iron pans it is obtained as a white solid, having a strong soapy feel, and acting corrosively upon the skin. It is one of the strongest alkalies. The reaction which yields it may be written as follows:

$$Na_2CO_3 + CaH_2O_2 = 2NaOH + CaCO_3.$$

Caustic soda is used in refining fats and oils, especially cotton-seed oil, and on a very large scale in the manufacture of soap. Soap is a compound of either alkali, with certain organic acids which are found in fats and oils. The soda-soaps are hard soaps, the potash-soaps are soft soaps. They are produced by boiling the alkali with the fat; and from a chemical stand-point they are just as truly salts of their respective acids as are the nitrates, sulphates, or chlorides. A hard soap made from an animal fat is mainly sodium stearate, $C_{18}H_{35}NaO_2$.

Sodium carbonate, Na_2CO_3, is a white solid having a strong alkaline reaction. The base is so strong, and the acid so weak, that in this salt the basic character predominates. It crystallizes with ten molecules of water of crystallization, Na_2CO_3, $10H_2O$, and occurs in commerce both in this form and dry. Crystallized sodium carbonate, or "sal soda," is the common washing-soda of the laundries. The dry carbonate is used in preparing other sodium compounds, and in enormous quantities in the manufacture of glass and soap. Hence its preparation constitutes one of the largest chemical industries.

Sodium carbonate is commercially manufactured by several processes; but only one, the process invented by Leblanc, is of sufficient importance to warrant description here.* First, sodium chloride is treated with sulphuric acid, yielding sodium sulphate and hydrochloric acid, thus:

$$2NaCl + H_2SO_4 = 2HCl + Na_2SO_4.$$

The operation is performed in a suitable furnace, about half a ton of salt being treated at a time; and the hydrochloric acid is in most establishments condensed by water and saved. The crude sodium sulphate is technically known as "salt-cake."

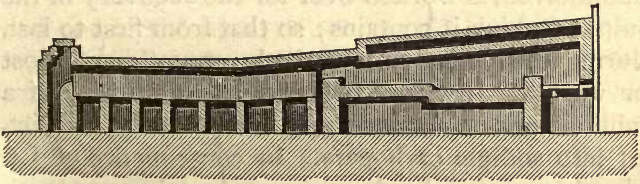

FIG. 41.—Black-ash Furnace.

The second stage of the manufacture consists in

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* Another process, the "ammonia-soda process," now bids fair to supplant Leblanc's method.

the conversion of the salt-cake into sodium carbonate, and is called the "*black-ash*" process. Ten parts of salt-cake, ten of limestone, in small fragments, and seven and a half of coal, are heated together in a reverberatory furnace until the mass fuses, when it is taken out to cool. Two reactions here take place; first, the carbon of the coal withdraws oxygen from the salt-cake, leaving sodium sulphide:

$$Na_2SO_4 + C_4 = Na_2S + 4CO.$$

The limestone (calcium carbonate) next reacts upon the sodium sulphide, forming by *double decomposition* calcium sulphide and sodium carbonate, as follows:

$$Na_2S + CaCO_3 = Na_2CO_3 + CaS.$$

By treating the black-ash with water, the sodium carbonate is dissolved out, and afterward, by evaporation, it is obtained in crystals. These, calcined, yield the dry carbonate, which is the soda-ash of commerce. The calcium sulphide, which remains undissolved, is worked over for the recovery of the sulphur which it contains; so that from first to last, during the entire process, little or nothing is lost or wasted. In Great Britain alone, at least half a million tons of common salt are annually converted into sodium carbonate. In consequence of Leblanc's process sal-soda now costs less than one tenth of what it did a century ago; and, of course, glass and soap have been proportionally cheapened. Although the whole world has been benefited by the invention, Leblanc himself was allowed to die in abject misery.

When the crystallized sodium carbonate is exposed to the action of carbon dioxide, sodium hydrogen carbonate, $NaHCO_3$, or "bicarbonate of soda" is produced. This is the common cooking-soda of the household, and an important constituent of all baking-powders. It is also used in medicine, and in the preparation of various effervescent drinks.

Only a few other sodium salts require especial mention here. The sulphate, Na_2SO_4, is important as salt-cake; and, crystallized, as $Na_2SO_4,10H_2O$, it is known as Glauber's salts, and has some medicinal value. The acid sulphate, $NaHSO_4$, is used in chemical analysis. The nitrate, $NaNO_3$, is found in large beds in Chili, Peru, and Bolivia, whence its commercial name of Chili saltpeter. It is used as a fertilizer, in the manufacture of nitric acid, and for the preparation of common saltpeter. Sodium thiosulphate, $Na_2S_2O_3, 5H_2O$, has already been mentioned on account of its use in photography; sodium hypochlorite, $NaCl_2O_2$, has some applications as a disinfectant; the chlorate, $NaClO_3$, is employed as an oxidizing agent in dyeing with aniline black; and one of the phosphates, $Na_2HPO_4, 12H_2O$, is an important laboratory reagent, and also of value medicinally. Borax, $Na_2B_4O_7, 10H_2O$, and sodium silicate or water-glass, have been sufficiently described in previous chapters.

POTASSIUM, although less widely diffused in nature than sodium, is still one of the most abundant elements. It is contained in most granitic rocks, whence it finds its way into the soil, from which it is extensively taken up by growing plants. Formerly its compounds were almost exclusively obtained from wood-ashes, whence the old name of vegetable alkali, as applied to its carbonate. To-day, great quantities of potassium salts are derived from the Stassfurt salt-beds.

There are two oxides of potassium, K_2O and K_2O_4. From the first, potassium hydroxide, KOH, or caustic potash, is derived. Practically, however, this important compound is prepared from potassium carbonate by treatment with milk of lime, just as in the preparation of caustic soda. It closely resembles the latter substance, and is used for similar purposes.

Potassium carbonate, K_2CO_3, is the familiar substance potash. The simplest mode of preparing this compound is to boil wood-ashes with water, and afterward to evaporate the solution. Until a few years ago, nearly all the potash of commerce was obtained from this source; but now a variety of other sources are available. First, potassium chloride and potassium sulphate are found in large quantities in the Stassfurt salt-beds. These are treated by Leblanc's process in just the same manner as the corresponding sodium compounds, and yield potassium carbonate by precisely similar reactions. Secondly, the residues left behind in the manufacture of beet-root sugar, yield annually some thousands of tons of potash. Thirdly, there is the most extraordinary source of all. Sheep, when feeding, take up large quantities of potassium salts from the soil. These are exuded in the perspiration, and remain adhering to the wool. When the wool is washed at some of the great European centers of the woolen industry, the wash-water is evaporated to dryness, and a substance known as "suint" is obtained. This, which contains the potassium salts of certain organic acids, is heated in iron retorts, giving off a fair quality of illuminating gas. From the charred residue, water extracts potassium carbonate. By this curious process, which splendidly illustrates the way in which chemistry utilizes seemingly worthless materials, at least a thousand tons of potash are annually made.

Potassium carbonate, when pure, is a white salt containing no water of crystallization. It has a strong alkaline taste and reaction, and is used for preparing other potassium compounds, and for the manufacture of glass and soft soap. By treatment with carbon dioxide, it yields a "bicarbonate," $KHCO_3$.

Potassium chloride, bromide, and iodide, are all white salts, which crystallize in cubes. The chloride is chiefly used, as above indicated, in the preparation of the carbonate; the bromide and iodide are important medicinally. The formulæ, potassium being univalent, are naturally KCl, KBr, and KI.

Two other salts of potassium are of great practical importance, the chlorate and the nitrate, $KClO_3$ and KNO_3. The properties of the chlorate, and its uses for making oxygen and in pyrotechny, have been sufficiently indicated in previous chapters. It is also used in medicine, for allaying inflammation of the throat, in calico-printing, and in the manufacture of matches.

Potassium nitrate, popularly known as saltpeter or as niter, is a salt which crystallizes easily in long, white prisms. It occurs naturally in the soil in many tropical countries, especially in Egypt and the East Indies, and is extracted easily by solution in water. It originates from the oxidation of organic matter rich in nitrogen, in presence of potassium compounds. In Sweden much saltpeter is prepared artificially by piling up animal refuse with lime, soil, and a little potash; and, after a proper period of time, leaching the mass with water. It is also made by double decomposition from the crude potassium chloride of Stassfurt and the cheaper Chili saltpeter.

$$KCl + NaNO_3 = NaCl + KNO_3.$$

It is used in the preservation of meat, and in the manufacture of gunpowder.

Gunpowder is a mechanical mixture of charcoal, sulphur, and saltpeter. A good average powder is composed, by percentages, as follows:

KNO_3,	75
C,	15
S,	10
	100

When gunpowder burns, there is a great and sudden evolution of gas; and to the expansion of the latter the force of explosion is due. A cubic centimetre of powder gives about 280 cc. of gas; and the reaction, which in reality is very complicated, is *approximately* represented by the subjoined equation: *

$$2KNO_3 + S + 3C = K_2S + N_2 + 3CO_2.$$

The total explosive force of a pound of gunpowder, expressed in mechanical terms, is equivalent

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* There is a good discussion of this subject in Roscoe and Schorlemmer's "Treatise on Chemistry," vol. ii, part i, pp. 81–88.

to a power of lifting a weight of 486 tons one foot high.

AMMONIUM, NH_4, is a compound radicle which is most conveniently studied in connection with the alkaline metals. It plays the part of a metal, and its salts in many respects are very similar to those of potassium. When ammonia, NH_3, is brought into contact with HCl, union takes place, and NH_4Cl is formed. So also, when ammonia is passed into water, the strongly alkaline solution may be regarded as having the formula NH_3, H_2O, or NH_4OH. In one compound, we have the chloride of NH_4, and in the other an alkaline hydroxide similar in character to KOH and NaOH. Like the latter hydroxides the ammonium hydroxide or caustic ammonia is capable of saturating the strongest acids, and of forming crystalline salts in which the NH_4 plays precisely the same part as K or Na. In NH_4, which has not yet been obtained by itself, an atom of quinquivalent nitrogen has four of its bonds of valency saturated; and by virtue of the one which remains it is univalent. For convenience, we may treat ammonium as if it were really a metal having an atomic weight of 18, and designate it by the provisional symbol Am.

Most of the ammonium salts are prepared by saturating aqua ammonia with acids; although in practice there are some exceptions. The chloride, AmCl, is a white salt which occurs in commerce in tough fibrous masses. It is purified by sublimation, being readily volatile. From its formula the density of its vapor should be $\frac{14 + 4 + 35.5}{2} = 26.75$; whereas experiment gives it a density only one half as great. That is, its vapor forms four volumes instead of agreeing with the two-volume law. This anomaly has been explained by showing that at high temperatures the compound NH_4Cl can not exist; but splits up into NH_3 and HCl, each represented by two volumes. On cooling, the parts recombine, again forming NH_4Cl. This splitting up so as to give an unusual vapor-density is called *dissociation*, and many examples of it are known. The explanation is not wholly theoretical, but rests upon solid experimental demonstrations.

Ammonium chloride has some medicinal use, is largely employed in dyeing, and is a source of other ammonium compounds. In soldering and tinning it serves to cleanse the metallic surfaces. Ammonium sulphate, Am_2SO_4, is important as a fertilizer; the nitrate, $AmNO_3$, is used in making nitrous oxide; and a phosphate of sodium, hydrogen, and ammonium, $NaHAmPO_4, 4H_2O$, microcosmic salt, is a useful reagent in blow-pipe analysis.

When hydrogen sulphide, H_2S, is passed into aqua ammonia, ammonium hydrosulphide, AmSH, is formed. There are also several sulphides of ammonium, of which Am_2S is the most typical. These compounds are much used as test reagents in chemical analysis.

EXPERIMENT 81.—Dissolve in water, in separate test-tubes, fragments of zinc sulphate, iron sulphate, copper sulphate, manganese chloride, arsenious oxide, and tartar emetic. Add to each solution a drop of ammonium hydrosulphide, and note the color of the precipitate. On adding an excess of the reagent, the arsenic and antimony precipitates will redissolve.

Ammonium carbonate is another salt which is used in medicine and as a reagent in analysis. It has a complicated formula, and occurs in commerce under the name of *sal-volatile.* It smells strongly of ammonia, and is often met with in the form of "smelling-salts."

From ammonia and ammonium a number of other strong bases are derived, which will be described in connection with organic chemistry.

CHAPTER XXI.

SILVER AND THALLIUM.

SILVER, which is also a univalent metal, is found in nature both free and in a great variety of compounds. The native metal, pure or nearly pure, sometimes occurs in quite large masses; but the more important ores of silver are compounds. Among them are found the chloride, bromide, iodide, sulphide, and telluride, and many double compounds containing the sulphide united with sulphides of arsenic and antimony. In some cases the silver seems to be merely an impurity, as in certain ores of copper and lead, from which the more precious metal also may be extracted.

Silver is obtained from its ores by a great variety of processes, concerning which a treatise on metallurgy may be consulted. Only two of them can be considered here. First, there is the amalgamation process, which is essentially as follows: The finely-powdered ore is roasted in a reverberatory furnace with a quantity of common salt, whereby the silver is converted into chloride. The mass is then mixed with water to a thin paste, and shaken up with scrap-iron in revolving casks for several hours. The iron withdraws the chlorine from the silver, thus:

$$2AgCl + Fe = FeCl_2 + Ag_2.$$

Mercury is next added, and the agitation is continued until an amalgam of silver and mercury is obtained. From this the mercury is distilled off, and the silver, often containing gold, remains behind.

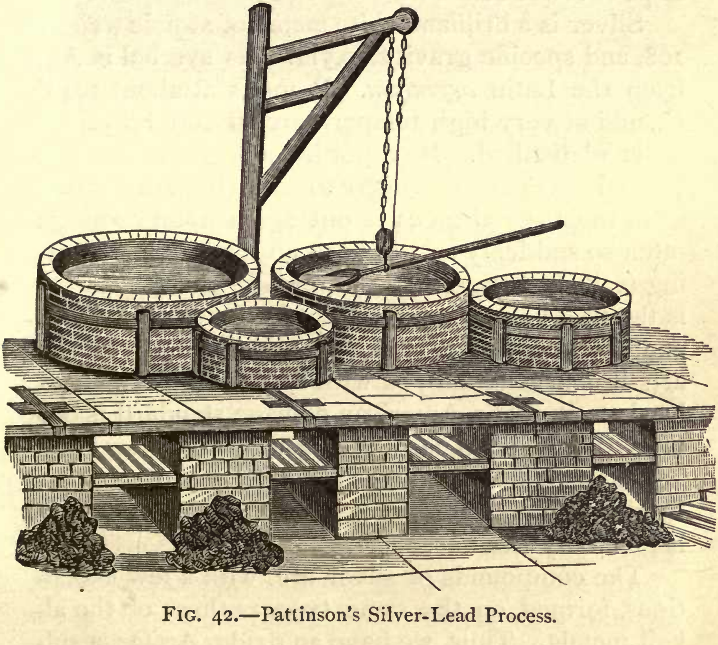

FIG. 42.—Pattinson's Silver-Lead Process.

Secondly, there is the Pattinson process, by which the traces of silver that often occur in lead-ores may be separated from the lead. The latter is first melted and allowed partially to cool; crystals of lead separate out, and are removed by a strainer, and a richer alloy is left behind. This is remelted, and the process of partial cooling and straining is continued until an alloy containing at least three hundred ounces of silver to the ton is obtained. This alloy is then *cupelled*—a process in which it is melted on a porous bed of bone-ash in presence of a blast of air. The lead is oxidized, the fused oxide is absorbed by the bone-ash, and at last a button of pure silver remains.

Silver is a brilliant white metal, of atomic weight 108, and specific gravity 10.512. Its symbol is Ag, from the Latin *argentum*. It melts at about 1040° C., and at very high temperatures it may be vaporized and distilled. Its vapor has a bright blue color. Melted silver absorbs many times its bulk of oxygen from the air, and gives it out again upon cooling; often so suddenly as to cause an explosive spattering (called *spitting*) of the semi-fluid metal. Silver is the best known conductor of heat and electricity, and is exceedingly malleable and ductile. In the arts it is usually alloyed with a little copper, which hardens it. The American coinage standard is 900 fine—that is, 1,000 parts of the metal used for coining contain 900 parts of silver to 100 of copper. English silver coins are 925 fine. Jewelers' silver is generally less fine.

The compounds of silver are, with a few exceptions, formed on the same type as those of the alkali metals. Thus, we have an oxide, Ag_2O; a sulphate, Ag_2SO_4; a nitrate, $AgNO_3$; and a chloride, AgCl. In general, the salts of silver do not contain water of crystallization. The sulphide, Ag_2S, is interesting as a natural ore, and on account of the ease with which it is produced artificially. The blackening of silver-ware is due to H_2S in the atmosphere; and the blackening of spoons by eggs is caused by the sulphur which the latter contain. Pass a bubble of H_2S into a solution of silver nitrate, and a black precipitate of silver sulphide will form.

The most important compounds of silver are the chloride and the nitrate. Some of their relations to each other and to the metal may be profitably studied by experiment.

EXPERIMENT 82.—Cover a small silver coin, either in a glass beaker, flask, or porcelain dish, with a mixture of half-and-half nitric acid and water. Upon heating, the coin will dissolve, and the solution will have a blue color due to the copper which is present. Add a solution of common salt, NaCl, in considerable excess, and shake vigorously. Silver chloride, which is insoluble, will be precipitated, while all the copper will remain dissolved. Filter, and wash the precipitate thoroughly by pouring water over it until the liquid runs through colorless. Transfer the silver chloride, still moist, to a porcelain dish, add some clippings of zinc, and cover the mixture with dilute sulphuric acid. By the action of the latter on the zinc, hydrogen will be evolved, which, at the instant of its liberation, *in the nascent state*, will withdraw chlorine from the silver chloride, forming hydrochloric acid, and setting the metal free. When all the zinc has been dissolved, silver will remain as a black, spongy mass, which may be either melted into a globule before the blow-pipe, or dissolved in nitric acid to form *pure* $AgNO_3$. From its colorless solution the latter compound is deposited in tabular, transparent crystals. This experiment shows, on a small scale, the exact method by which the officers of a mint or silver-refinery prepare pure silver from crude bullion.

The formation of silver chloride in the foregoing experiment is according to the equation—

$$AgNO_3 + NaCl = NaNO_3 + AgCl,$$

and well illustrates what is called *double decomposition.* Silver and sodium change places, as also do the nitric-acid radicle and chlorine; and two new salts result from the mutual transfers. We have already met with several examples of this sort of chemical change, and we shall meet with many more as we go on. They all come under one of two laws, which, having been first announced by Berthollet, are known as *Berthollet's laws*, and are as follow: 1. *Whenever two substances in solution together are capable of exchanging atoms so as to form a compound insoluble in the solvent employed, that compound will be produced and deposited as a precipitate.* 2. *Whenever two substances in mixture are capable of exchanging atoms so as to form a compound which is gaseous at the temperature of the experiment, that compound will be evolved as a vapor or gas.* The case in point illustrates the first law; the second may be exemplified by heating together ammonium chloride and hydrogen sodium carbonate. Ammonium carbonate, which is volatile, will be set free, and sodium chloride will remain.

$$NaHCO_3 + AmCl = NaCl + AmHCO_3.$$

In the actual experiment the NH_4, HCO_3 splits up into $NH_3 + CO_2 + H_2O$. This particular mixture has been proposed, and slightly used, for a baking-powder.

Silver chloride, as obtained in Experiment 82, is a white, curdy precipitate which darkens on exposure to light. If potassium bromide or iodide be used in place of common salt, silver bromide or iodide will be thrown down. The latter is yellow, the bromide is yellowish white. All these compounds are sensitive to light, and they are therefore of great importance in the art of photography.

We have already seen, in studying the formation of hydrochloric acid, that light may bring about chemical union. It may also effect chemical decomposition; and this is especially the case with most of the salts of silver. All, or nearly all of them, when in contact with organic matter, are blackened by light—most where the light is strongest, less where it is weaker. This fact is the foundation principle of photography,* which, in its commonest form, is essentially as follows:

A glass plate is first coated with a film of collodion, which is prepared by dissolving gun-cotton in a mixture of alcohol and ether, and adding to it certain bromides or iodides. The plate is next dipped into a solution whereof silver nitrate is the chief ingredient, and either the bromide or iodide of silver is precipitated in the collodion-film. Having been thus prepared in a dark room, the plate is transferred to the photographic camera, and the image of the scene or object to be photographed is allowed to fall upon it. Where the object is light, the plate is strongly affected; where it is

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* Captain Abney's "Treatise on Photography" is one of the best of the smaller works on this subject; Vogel's "Chemistry of Light and Photography" ("International Scientific Series," vol. xiv) is also very good.

dark, the action is slighter; so that the picture which is produced has all its lights and shadows reversed, and is called a "negative." When first taken from the camera, the plate shows no signs of alteration; but the image is brought out by pouring over the plate a chemical solution known as the developer. For this purpose various substances are used, ferrous sulphate being the commonest.* Finally, the plate is washed with a solution of sodium thiosulphate, which dissolves out the silver salts which have been unattacked, and the picture is thus rendered permanent. In "printing" from this negative, a sheet of paper is rendered sensitive by silver nitrate, and exposed underneath the plate to the action of strong sunlight. Where the negative is dark the paper remains light, and *vice versa;* so that an image which is correct as to lights and shadows is produced. This, too, is "fixed" by sodium thiosulphate, and, after some little details of finishing, the photograph is done.

EXPERIMENT 83.—Soak a sheet of white paper in a solution of silver nitrate. Place over it a piece of lace or a fern-leaf, cover it by a sheet of glass, and expose it to the sunshine until all the uncovered portions are darkened. Wash it in a dark room or closet, first with a solution of sodium thiosulphate, and afterward with pure water, continuing the latter until the rinsings no longer have a sweetish taste. A perfect copy of the lace pattern or leaf will remain as a photographic print on the paper.

Silver nitrate, which is always prepared by dis-

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* The theory of the action of the developer is somewhat obscure, and would be out of place in this treatise.

solving silver in nitric acid, occurs in commerce in two forms: First, we find it in large, transparent, tabular crystals, in which form it is used for various laboratory purposes, by the photographers, and in the art of electroplating; second, the fused salt is cast in small, round sticks, which are used by physicians under the name of "lunar caustic." It is applied to the cautery of inflamed surfaces.

When a little potassium cyanide, KCN, is added to a solution of silver nitrate, a precipitate of silver cyanide, AgCN, closely resembling the chloride, is formed. Upon the addition of more KCN, the precipitate redissolves, and a solution is produced which is much used in silver-plating.* In such a solution, the preparation of which is subject to many variations, the object to be plated is immersed, together with a bar, rod, or plate of pure silver. The latter is connected by a wire with the negative element of a battery, while the object to be plated is connected with the other pole. When the current passes, electrolysis takes place, and silver is deposited upon the object in a thin, coherent film. At the same time silver is dissolved off from the plate at the opposite pole. The process continues until the plating has acquired whatever thickness may be demanded; afterward the plated article is washed and polished. The same general method, but with different solutions, is employed in plating with gold, copper, platinum, or nickel.

THALLIUM, atomic weight 204, is one of the very rare metals. It was discovered in 1861 by Crookes,

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* For full details as to solutions and processes, see Gore's "Electro-Metallurgy."

with the aid of the spectroscope, and in its general properties it strongly resembles lead. Its compounds give a brilliant green color to flame, and are mostly poisonous. It forms two sets of salts—the *thallious* and *thallic* compounds; behaving like a univalent element in the first, and being trivalent in the second. It occurs as an impurity in iron pyrites and in native sulphur, and is usually obtained from the flue-dust of sulphuric-acid works.

CHAPTER XXII.

CALCIUM, STRONTIUM, AND BARIUM.

THE bivalent metals are quite numerous, and form several well-defined sub-groups. In one of these we find the three closely allied metals whose names head this chapter.

	Atomic weight.	Specific gravity.
Calcium, Ca	40	1.58
Strontium, Sr	87.5	2.58
Barium, Ba	137	3.75

In general, strontium and its compounds have properties nearly midway between those of the other two metals. For instance, strontium sulphate is less soluble in water than calcium sulphate, and more so than barium sulphate; and in specific gravity it also lies between the two. In short, if we know the properties of two corresponding salts of barium and calcium, we can make a close guess as to what the properties of the similar strontium salt will be. The metals themselves are unimportant, and difficult to obtain. Calcium is yellow, strontium yellowish, barium white. All three are fusible only above a red heat, all oxidize easily in the air, all are malleable and ductile.

CALCIUM is one of the most abundant of elements. As carbonate we find it in nature in the form of limestone, marble, chalk, coral, marl, etc. It enters into the composition of many silicates; the sulphate, fluoride, and phosphate are abundant minerals; and the phosphate is also an important ingredient of plants and of bones.

Calcium oxide, CaO, is commonly known as quicklime. It is always prepared by heating the carbonate, which is decomposed in accordance with the following reaction:

$$CaCO_3 = CaO + CO_2.$$

On a large scale, limestone is burned in a lime-kiln (Fig. 43), and the lime remains behind. It is a white, infusible solid, which unites violently with water, evolving great heat, and forming the hydroxide, CaH_2O_2. The latter formula may also be written $Ca(OH)_2$, to illustrate the bivalency of the metal.

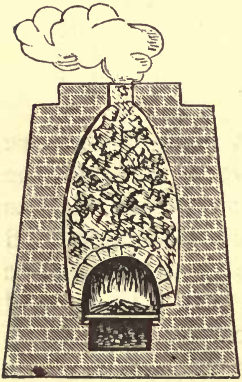

FIG. 43.—Lime-Kiln.

Calcium hydroxide, or slaked lime, is a very useful compound. The heat attending its formation may be observed by sprinkling a little cold water over a lump of lime and noting that steam is evolved. Fires are often caused by the accidental contact of water with lime which has been stored in leaky buildings. Under such circumstances, in a closed space, the heat may be sufficient to kindle wood.

Just as sodium hydroxide is called caustic soda, so calcium hydroxide is often called caustic lime. It has a strong alkaline reaction, neutralizes acids, and attacks organic matter vigorously. It is often used as a fertilizer, inasmuch as it helps to rot organic substances in the soil; and in tanneries it is applied to hides to aid in the removal of hair. As milk of lime—that is, suspended in water—it serves as whitewash; and it is also used in purifying coal-gas, in making bleaching-powder and the caustic alkalies, and for a great variety of other chemical purposes. But the larger uses of slaked lime are in the preparation of mortars and cements. Mortar is made by mixing lime with water and sand; for interior plastering hair is added, to bind the mass together. When first mixed, mortar is soft and pasty; on drying it hardens, absorbs carbon dioxide from the air, and forms a substance which in time becomes almost as compact as stone. In very old brick-work, the mortar is often harder and stronger than the bricks themselves. *Hydraulic lime*, which forms a cement capable of hardening under water, is made by burning a limestone mixed with clay.

The extensive occurrence of calcium carbonate in nature has already been noticed. In its purest state this substance forms transparent crystals, which vary remarkably in character. One variety is known as Iceland-spar (Fig. 44), and is doubly refracting—that is, a line or object seen through it appears to be doubled. Iceland-spar is much used in instruments for studying polarized light. In pure water calcium carbonate is very slightly soluble; more so in water containing carbonic acid.

EXPERIMENT 84.—Into a test-tube filled with lime-water pass a bubble of carbon dioxide. Calcium carbonate will be thrown down as a white precipitate, but, if a stream of the gas be passed in for a longer time, it will again dissolve. Upon boiling the clear solution the excess of CO_2 will be driven off, and $CaCO_3$ will be reprecipitated.

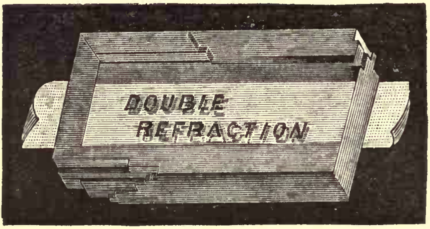

FIG. 44.—Double Refraction.

It is by this solvent action of water charged with carbon dioxide that great limestone caverns, like the Mammoth Cave of Kentucky, are formed. From the roof of such a cave, especially during its period of formation, water continually drips. Each drop, in falling, leaves behind a particle of its dissolved limestone, and deposits another particle upon the floor beneath. Thus, in the course of ages, a stalactite grows slowly downward, like a stone icicle, from above; while from below a stalagmite rises gradually to meet it. If the process continues long enough, a column of semi-transparent calcium carbonate is the result.

Calcium sulphate, crystallized with two molecules of water, occurs abundantly in nature as gypsum, $CaSO_4, 2H_2O$. In white, translucent masses, it is used as an ornamental stone, and is known as *ala-*

baster; in regular, transparent crystals, it is called *selenite*. Gypsum is somewhat important as a fertilizer; and, when deprived of its water by calcination, it forms plaster of Paris. The latter substance, when mixed to a thin paste with water, reabsorbs the two molecules which were lost on calcination, and "sets" to a compact, solid mass. In solidifying it also expands; and to this fact is partly due its value in making casts. When poured into a mold, it forces its way into every crack and crevice, and thus a perfect copy is insured.

Like calcium carbonate, calcium sulphate is slightly soluble in water; and in natural waters both compounds often occur. Such waters are popularly known as "hard" waters, and are objectionable for washing purposes or for use in the steam-boiler. In the latter case, the lime-salts are liable to be deposited on the sides of the boiler as a hard, coherent coating, called boiler-crust or boiler-scale, which, being a non-conductor of heat, causes great waste of fuel. In the laundry, lime-salts react upon the soap which is used, and insoluble lime-soaps are precipitated; so that no good soapy effect can be produced until all the calcium compounds have been eliminated.

Calcium fluoride, CaF_2, has already been referred to in connection with fluorine. It is a mineral which crystallizes in cubes, often brilliantly colored, and is useful in the preparation of hydrofluoric acid. The nitrate, $Ca(NO_3)_2$, is found in the soil of some caves, and when abundant may be profitably treated with potassium carbonate, and made a source of saltpeter. The phosphate, $Ca_3(PO_4)_2$, is found in bones, and also, combined with a little fluoride or chloride, in great beds as a mineral. It is valuable as a fertilizer; and, when treated with sulphuric acid, it yields the so-called "superphosphate," $CaHPO_4$, which is much used in agriculture.

Calcium hypochlorite, chloride of lime, or bleaching-powder, has already been described. Calcium chloride, $CaCl_2$, which is prepared by dissolving chalk or marble in hydrochloric acid and evaporating to dryness, is a white, soluble compound much used in the laboratory. It absorbs moisture with great avidity; enough in damp air to actually dissolve itself; and is, therefore, of great value in drying gases. It is also employed in making some kinds of artificial stone. The crystallized salt, $CaCl_2, 6H_2O$, mixed with pounded ice or snow, gives a powerful freezing mixture; and with it a temperature as low as $-48.5°$ has been obtained.

STRONTIUM, as compared with calcium, is rare and comparatively unimportant. Its sulphate and carbonate occur as beautifully crystallized minerals. Its compounds give a rich red color to flame, and on this account its nitrate, $Sr(NO_3)_2$, and its chlorate, $Sr(ClO_3)_2$, are used in the red-fire mixtures of the pyrotechnist. Most of these mixtures contain sulphur, and therefore smell badly when burning; but the following experiment may be tried in a room:

EXPERIMENT 85.—Take two parts of potassium chlorate, two of strontium nitrate, and one of shellac. *Powder them separately*, and finely, and mix on paper with as little friction as possible. Kindle the mixture in any convenient vessel, and it will give the brilliant strontium-flame. The ingredients should be weighed out, and all should be scrupulously dry.* If barium nitrate be used in place of the strontium salt, a green-fire mixture will be made.

BARIUM is much more plentiful than strontium; but, like the latter metal, it occurs mainly as sulphate and carbonate. It is also found in a few rather uncommon silicates. Several of its compounds have practical interest. The chloride, $BaCl_2$, $2H_2O$, and the carbonate, $BaCO_3$, are useful reagents in qualitative analysis; and, as above indicated, its nitrate is employed by the pyrotechnist in making green fire. There are two oxides of barium, BaO and BaO_2, and these are easily transformable, the one into the other. Upon this fact a "regenerative" process for making oxygen has been based. The monoxide, BaO, heated in a stream of air, is converted by direct oxidation into BaO_2. The latter, heated more strongly, gives up its extra atom of oxygen, leaving BaO ready to be recharged in another air-current. The operation may be repeated indefinitely. The BaO serves as a carrier by which oxygen may be withdrawn from the atmosphere and transferred to a gas-holder.

Barium sulphate, $BaSO_4$, is noted for its insolubility. Add sulphuric acid or a solution of any other sulphate to a solution containing barium, and $BaSO_4$ will be thrown down as a heavy white powder. Hence sulphuric acid serves as a test for barium, and *vice versa*. The precipitated compound is somewhat used as a white paint, under the name of *blanc fixe;* and the natural sulphate, which is commonly called barytes or heavy spar, is ground

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* A good list of recipes for different colored fires is given in Sadtler's "Chemical Experimentation," p. 202. The book is a useful one for either pupils or teachers.

up as an adulterant for white-lead. By heating the sulphate with charcoal, the sulphide, BaS, is produced. This substance, exposed to a strong light, is afterward luminous in the dark. The sulphides of calcium and strontium have similar properties, and from either of the three a luminous paint may be made.

CHAPTER XXIII.

SPECTRUM ANALYSIS.*

WHEN a beam of sunlight passes through a glass prism, and falls upon a white screen, colors are produced, and the unaided eye readily distinguishes at least seven tints. These are red, orange, yellow, green, blue, indigo, and violet, and are popularly known as the seven primary colors. If the prism is placed in a dark chamber, and the light is admitted only through a narrow slit, the colors arrange themselves in a long band, side by side, with the red at one end and the violet at the other, and the remaining tints occupying their proper order between. In the sunbeam these colors are all mixed together, and the effect of the prism merely is to separate them, by virtue of their differences in refrangibility.

Suppose now that, instead of sunlight, some colored flame be studied with the prism, what sort of a color-band or *spectrum* shall we obtain? In every case we shall have, not a continuous band of colors, but one or more bright-colored lines, sepa-

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* In a treatise on chemistry this subject can be considered only on its chemical side. The physical theory of the spectroscope, the nature of luminous waves, etc., can be properly studied only as a branch of physics.

rated from each other by dark spaces; and these lines will be absolutely characteristic of the substance to which the tint of the flame is due. A compound of sodium will give one bright-yellow line; potassium, a red and a violet; thallium, a green line; strontium, a cluster in the red and orange, and one brilliant line in the blue; barium, a number of lines near together, and mainly in the green and yellow portions of the spectrum; lithium, a very rich line in the red, etc. There are also some fainter lines which need not be mentioned here; and occasionally lines, which seem at first to be single, prove when magnified to consist of several closely huddled together. The yellow line of sodium, for instance, is really double. In no case does any element give a line belonging to any other; so that if we insert any substance in a flame and examine its spectrum, we can determine at once which of the above-named elements it contains. This method of examination is called *spectrum analysis;* and it is well illustrated by the colored chart of spectra which is the frontispiece to this volume.

In order that spectra may be conveniently studied, an instrument called the *spectroscope* has been devised. This, like most other great inventions, grew up step by step, one discoverer after another adding some point or detail; but the honor of completing and perfecting the instrument is chiefly due to Professor Bunsen, of Heidelberg in Germany. In its simplest form it is constructed as follows (Fig. 45):

A prism and two small telescopes are mounted upon a circular metallic plate and stand, as shown in the illustration. One telescope, which serves for receiving the light to be examined, is closed at its outer end by two metallic knife-edges, which may

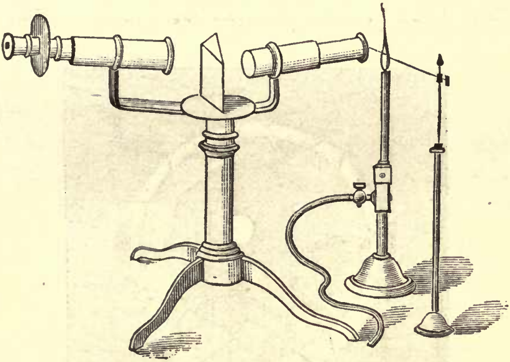

FIG. 45.—One-Prism Spectroscope.

be moved nearer together or farther apart, and which furnish the narrow slit as previously indicated. The second telescope is used for observing the spectrum. The light enters the slit, passes through the collecting-telescope, and falls upon the prism. There it is refracted and dispersed, and is seen through the observing eye-piece as the long band which was described in a previous paragraph. In nice instruments the observing eye-piece contains a pair of cross-hairs, and is movable, with its telescope, from side to side; and the metallic plate which supports it is provided with a graduated circle. Then, by moving the telescope so as to bring each spectral line exactly across the intersection of the cross-hairs, its position relatively to other lines may be accurately measured. With these additions the spectroscope becomes also a *spectrometer*, and is a most convenient instrument for many optical investigations. Instead of one prism, a spectroscope may contain several prisms, and so be greatly increased in power (Fig. 46).

Another convenient form of instrument is the *direct-vision spectroscope.* In the ordinary spectroscope the light is so refracted that the two telescopes form an angle with each other; and it is often a tedious matter to adjust them relatively to the prism in the proper position. In the direct-vision spectroscope the prisms, which may number three, five, seven, or nine, are arranged as shown in Fig. 47, and no adjustment is necessary. Such spectroscopes are now made very cheaply, and small enough to be carried in the vest-pocket. For many purposes they are very handy and useful.

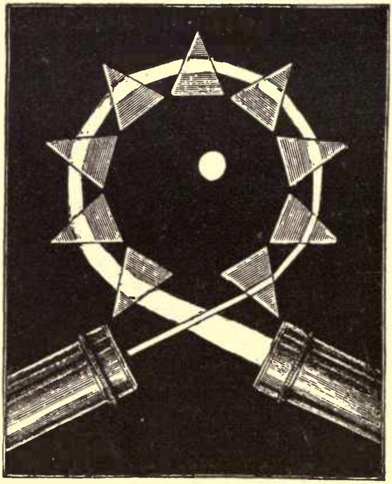

FIG. 46.—Diagram of a Train of Prisms, with Telescopes.

In the laboratory the spectroscope is mainly used for detecting Li, Na, K, Cs, Rb, Tl, Ca, Sr, Ba, B, or Cu; all of which substances impart definite colors to a gas or alcohol flame. The usual plan is to put a little of the substance under examination upon a piece of clean platinum wire, and insert it in the flame of a Bunsen gas-burner. Then, almost at a glance, whatever spectra may be present can be recognized. Some of the tests are inconceivably delicate—for example, $\frac{1}{180000000}$ of a grain of sodium, or $\frac{1}{6000000}$ of a grain of lithium, will reveal its presence immediately. Several of the rarer metals have been discovered by means of the spectroscope—namely, cæsium, rubidium, thallium, indium, and gallium. Cæsium and rubidium were discovered by Bunsen himself, shortly after the invention of the instrument. He applied his spectroscope to the examination of a mineral water, and observed certain lines which belonged to no known element. He at once inferred that some new element must be present; and, carefully searching, obtained the chlorides of the two metals. At the high temperature of the electric arc all the elements give characteristic spectra, and most of them have been carefully mapped and examined.

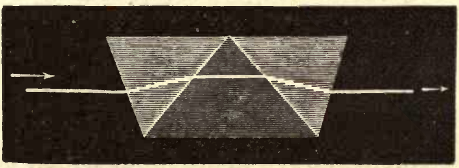

FIG. 47.—Section of a Direct-vision Spectroscope.

Another laboratory use of the spectroscope is in the identification of dissolved coloring-matters. If a beam of sunlight be passed through a solution of blood, cochineal, logwood, etc., a red light will be transmitted; other solutions transmit green, yellow, or blue tints mainly. If the transmitted light be examined with the spectroscope, certain parts of the complete spectrum will be found to be blotted out, and what is called an *absorption spectrum* will be seen. Such a spectrum is in most cases characteristic of the coloring-matter which produces it, and at once reveals the presence of the latter. The artificial color of an adulterated red wine may thus (with some limitations) be detected.

Whenever we have a spectrum consisting of bright lines with dark spaces between, it is produced by heated matter in the condition of a gas. All the elements above mentioned, which color the Bunsen flame, do so in the form of compounds which are gaseous at its temperature. The other elements, as was already stated, require much more elevated temperatures for the production of bright-line spectra.

If we study the light emitted by highly incandescent solids, such as the carbon of an electric arc or the lime cylinder in the oxyhydrogen-flame, we shall find that it gives a spectrum without lines, and brilliantly continuous from the red end to the violet. In the spectrum of sunlight, however, we have something different still—namely, a continuous spectrum intersected by a vast number of fine black lines, each of which occupies a fixed and definite position.* These lines were first described by Wollaston; and later they were carefully mapped by Fraunhofer;

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* Dark lines running *lengthwise* of the spectrum often confuse the beginner. They are due to dust-specks on the slit of the spectroscope.

they are now known as Fraunhofer's lines. Each of them corresponds in position exactly with one of the bright lines obtainable from a chemical element; for example, Fraunhofer's line "D," in the yellow, coincides precisely with the sodium-line, and, like the latter, is really double. What does this mean? The explanation, discovered by the joint labors of Professors Bunsen and Kirchhoff, is simple, and is an application of the physical law that *substances when cold absorb the same rays which they give out when hot.*

Let us consider a special case arising under this law. Suppose we arrange a spectroscope as in Fig. 48, and place in front of the slit a strong light capable of giving a continuous spectrum. Now between this light and the slit interpose a layer of sodium vapor, produced by heating a little metallic sodium in an iron spoon. The part of the spectrum corresponding to the sodium-line will be absorbed, and a dark line will be seen in its place. That is, sodium vapor absorbs the yellow ray which more intensely heated sodium vapor emits. This is commonly

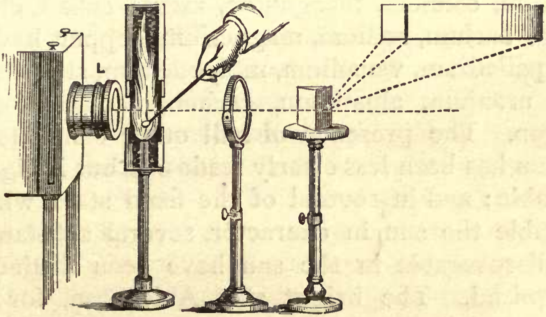

FIG. 48.—Reversal of Sodium-line.

known as the *reversal of the sodium-line;* and the lines of other elements may be similarly reversed. The spectrum of sunlight is merely a continuous spectrum, with the reversed lines of over twenty of the chemical elements distributed in their proper places through it. The conclusion is, that the sun contains these elements in the gaseous condition; and through such a gaseous envelope the light of the solid or liquid interior is transmitted. In short, by means of the spectroscope we can analyze the heavenly bodies, and tell of what substances they are composed.

In the solar spectrum, so far, lines belonging to the following elements have been identified: iron, titanium, calcium, manganese, nickel, cobalt, chromium, barium, sodium, magnesium, copper, hydrogen, palladium, vanadium, molybdenum, strontium, lead, uranium, aluminum, cerium, cadmium, and oxygen. The presence of still other elements in the sun has been less clearly made out, but is highly probable; and in several of the fixed stars, which resemble the sun in character, several substances not discoverable in the sun have been distinctly recognized. The bright star Aldebaran, for instance, contains hydrogen, sodium, magnesium, calcium, iron, *antimony*, *mercury*, *bismuth*, and *tellurium.*

At various points in the heavens are seen faint clouds of light, called nebulæ. Some of them are star-clusters, so distant that only a powerful telescope can recognize their true character; and such nebulæ give regular star-spectra. Others, however, when examined with the spectroscope, prove to be immense clouds of incandescent gas, and give a bright-line spectrum indicating hydrogen. This fact has a curious theoretical importance. It is commonly held by scientific men that the solar system was once a vast nebula, which gradually cooled and condensed into its present condition; and a great deal of evidence, physical and mathematical, can be cited in favor of this *nebular hypothesis*. In the heavens we see all stages of development—from the nebula itself, down to the hotter stars, the sun, and the solid planets; and accompanying this progression, we find a steady increase in chemical complexity. The nebulæ contain but one or two elements; the whitest and hottest stars a few more; stars like our sun a larger number still; and at last we find the earth with its multitude of compound bodies. From these facts we arrive at once at a startling conclusion, which, though not yet absolutely proved, is sustained by many lines of evidence, and is yearly becoming more and more probable; namely, that the evolution of planets from nebulæ has been accompanied by an evolution of the chemical elements from still simpler forms of matter; and that matter itself, like force, instead of being many different things, is really at bottom, in the final analysis, one.*

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* The student who cares to pursue the subject of celestial spectroscopy further may profitably begin with two volumes in the "International Scientific Series": Young's work on "The Sun," and Lockyer's "Studies in Spectrum Analysis."

CHAPTER XXIV.

GLUCINUM, MAGNESIUM, ZINC, CADMIUM, AND MERCURY.

ALTHOUGH the metals described in this chapter are all bivalent, they do not form as definite a natural group as some that we have been considering. Magnesium and zinc, indeed, are very closely related; so are zinc and cadmium; and, though less strikingly, so also are cadmium and mercury. But between magnesium and mercury, except as regards valency, the resemblances are quite remote.

GLUCINUM, often called *beryllium*, is a rare metal of specific gravity 2.1, and an atomic weight of 9. It is found in a few minerals, among which the beryl and the chrysoberyl are the only important species. The beryl is a silicate of glucinum and aluminum, and varies in color from white to yellow, and bluish to deep green. It is valuable as a gem; the bluish variety being known as aquamarine, and the green variety as the emerald. The salts of glucinum are all formed on a simple bivalent type, and in their outward properties have some resemblance to the compounds of trivalent aluminum. The oxide, GlO, the chloride, $GlCl_2$, and the sulphate, $GlSO_4$, are good examples of their chemical structure.

MAGNESIUM, atomic weight 24, is one of the more abundant elements, and forms an important part of the earth's crust. It occurs in many silicates, such as talc and serpentine; and in dolomite, a double carbonate of magnesium and calcium. The last-named species forms whole mountain ranges, and is often confounded with limestone. Some of its varieties resemble marble. Magnesium minerals frequently have a soapy feeling, as in soapstone, and so may be recognized by touch. Salts of magnesium are found in sea-water, and in many mineral springs.

The metal itself is usually prepared by heating the chloride with sodium; thus:

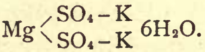
$$MgCl_2 + Na_2 = Mg + 2NaCl.$$

It is bluish-white, fusible at low redness, volatile at higher temperatures, and has a specific gravity of 1.75. It is easily combustible, and burns with an intensely brilliant light, emitting dense, white smoke-clouds of its solid oxide, MgO. It is commonly sold in the form of wire or ribbon, and may be kindled with a common match. Its light gives a continuous spectrum, but is brightest toward the violet end, and abounds especially in those rays which possess chemical activity. On this account it is available for photographic purposes; and is actually so used as a source of illumination in photographing the interior of caverns.

The compounds of magnesium are quite simple. The oxide, MgO, also known as *magnesia*, is a white powder somewhat used in medicine. Its popular name well illustrates a common method of abbreviating the names of oxides; as, for example, SiO_2, silica; Na_2O, soda; K_2O, potassa; BaO, baryta; SrO, strontia; Al_2O_3, alumina, etc. The superior convenience of these names over such terms as silicon dioxide, barium monoxide, etc., is evident. Magnesia unites readily with water to form a hydroxide, $Mg(OH)_2$, which occurs naturally crystallized as the mineral brucite. The carbonate, $MgCO_3$, is also found as a mineral, magnesite; and, artificially precipitated in union with hydroxide, as the *magnesia alba* of pharmacy. The double carbonate, $MgCO_3 + CaCO_3$, has already been referred to as dolomite.

The most important salt of magnesium is the sulphate, $MgSO_4, 7H_2O$. It was originally found in a spring at Epsom, England—whence the common name of Epsom salts. It is now prepared by treating either magnesite or dolomite with sulphuric acid, and evaporating the solution to the crystallizing point. It is a useful reagent in chemical analysis, and is a common household medicine.

The water of crystallization in magnesium sulphate deserves especial study. If the salt be heated to about 120° C., six molecules of its water are expelled; but the seventh molecule is retained with great tenacity up to a temperature of nearly 200°. This molecule, therefore, is differently combined from the others, and is known as *water of constitution*. It may be replaced by other sulphates; as, for example, K_2SO_4, yielding the double sulphate $MgSO_4, K_2SO_4, 6H_2O$.



$$Mg\begin{array}{l}\diagup SO_4-K\\ \diagdown SO_4-K\end{array} 6H_2O.$$

This compound is the type of an important class of double salts which result from the union of the alkaline sulphates with the sulphates of magnesium, zinc, iron, cobalt, nickel, and copper. These salts show that there is some relationship between magnesium and the last four metals.

ZINC, though far less abundant than magnesium, is more familiar as a metal. It is found in many minerals; but its chief ores are the oxide, zincite; the sulphide, zinc blende; the silicate, calamine; and the carbonate, smithsonite. These, in smelting, are first roasted, and then heated in either earthenware tubes or fire-clay crucibles with coke or charcoal. Zinc is set free, and distilled off into suitable vessels. It is finally remelted and cast into bars, which are known commercially as spelter. Sometimes the zinc-vapor is condensed in the form of zinc-dust, which is of use in some of the operations of organic chemistry. A mixture of zinc-dust and sulphur may be used to illustrate chemical

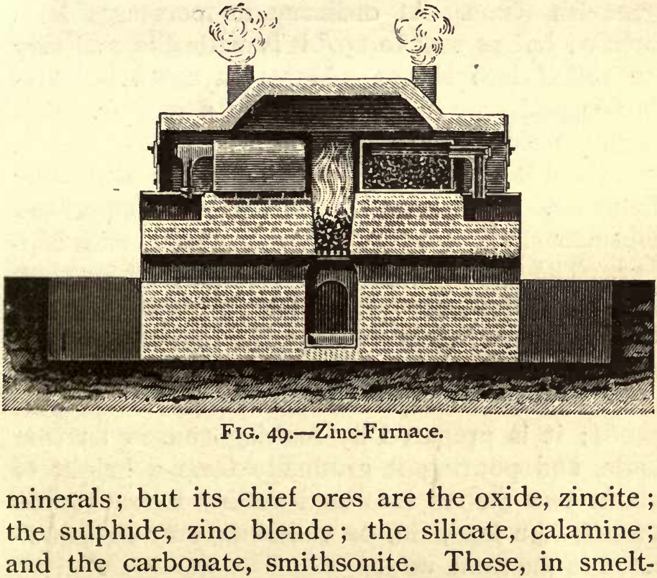


FIG. 49.—Zinc-Furnace.

union, as in Experiment 1. It can be kindled with a match and burns almost like gunpowder, leaving a residue of yellowish-white sulphide.

Zinc is a bluish-white metal of atomic weight 65, and a specific gravity from 6.8 to 7.3. It melts at 423°, and boils at 1,035°. It is slightly combustible, especially in thin sheets, and burns with a greenish flame. At ordinary temperatures it is brittle; but at 125° to 150° it is malleable, and may be rolled into sheets. At 205° it again becomes brittle, and may be pulverized in a mortar. It is largely used as sheet-zinc, for fire-screens, roofing, etc.; and it forms the positive plate in all voltaic batteries. Brass is an alloy of zinc and copper, and German silver consists of zinc, nickel, and copper. The so-called galvanized iron, used for roofing, cornices, window-caps, water-pipe, etc., is merely iron which has been dipped in melted zinc, and so coated with the latter. Granulated zinc is the most convenient form of zinc for laboratory purposes; it is prepared by melting zinc in an iron ladle, and pouring it gradually from a height of about two metres into cold water. Other fusible metals, like lead, tin, or cadmium, may be granulated in the same way.

Chemically, the compounds of zinc resemble those of magnesium. The oxide, ZnO, is white when cold, yellow when hot. A large deposit of it occurs at Franklin and Sterling, New Jersey, in red masses which owe their color to manganese as an impurity. The pure zinc oxide is important as a white paint, which is not discolored by atmospheric agencies. Zinc sulphide, ZnS, is often produced in the laboratory as a white precipitate, by adding ammonium sulphide to a solution of any soluble zinc-salt. It occurs in nature as a very common crystalline mineral, but is generally colored yellow, brown, or black, by impurities. The chloride, $ZnCl_2$, is a pasty solid, which is prepared by dissolving zinc in hydrochloric acid and evaporating to dryness. It is used in surgery as a caustic, and by tinners for cleansing tin-plate previous to soldering. It is also used on a large scale as an antiseptic, in the preservation of wood from decay. The process, which, from the name of its inventor, is called Burnettizing, consists in inclosing the wood in strong iron cylinders, pumping out the air by a powerful steam-pump, and then allowing the solution of zinc chloride to flow in under very heavy pressure. The wood is thus completely permeated by the preservative, and will last for years without rotting. Copper sulphate, mercuric chloride, coal-tar, creosote, etc., are also applied to wood in the same way and for the same purpose.

Zinc sulphate, $ZnSO_4, 7H_2O$, also called white vitriol, resembles magnesium sulphate very closely. It forms similar double sulphates, and its water of crystallization behaves in the same way. Its uses are chiefly medicinal, although in large doses it is poisonous. Applied externally in weak solutions, it quiets local inflammation; and it is especially used in treating diseases of the eye. Most of the so-called "eye-waters" are merely preparations of zinc sulphate.

CADMIUM, atomic weight 112, is a rare metal which is chiefly found as an impurity in zinc. It is bluish-white, brilliant, and of specific gravity 8.6. It melts at 320° C., and boils at 860°, forming a vapor having only half the density indicated by its atomic weight. Hence its molecule consists of a *single* atom. Cadmium is used in making certain fusible alloys,* and in preparing a few compounds. The iodide, CdI_2, is employed to some extent in photography; and the sulphide, CdS, is a brilliant yellow precipitate which is much prized by artists as a pigment.

MERCURY, or quicksilver, being the only metal liquid at ordinary temperatures, has always been an object of both popular and scientific interest. It is found in nature in the free state, and also in several ores; but only one of the latter, cinnabar, HgS, has any practical importance. It is extensively mined in Spain, Austria, China, Mexico, and Peru; but fully two thirds of the whole annual mercury-yield of the world comes from a few localities in California. From cinnabar the metal is easily extracted by a process of roasting with lime. The mercury volatilizes, and is condensed in suitable chambers or pipes. It is purified by straining through linen, and is sent into commerce in strong bottles made of wrought-iron.

The specific gravity of mercury, at 0°, is 13.596. At $-39.5°$ it solidifies to a malleable mass, of specific gravity 14.19. At 357° it boils, yielding a vapor of density 100, its atomic weight being, as in the case of cadmium, twice as great, or 200. Hence the mercury molecule consists of one atom. Pure mercury does not tarnish in the air until heated above 300°, when it slowly unites with oxygen to form the red oxide. It combines directly with chlorine, bromine, iodine, and sulphur, and dissolves in

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* Described under bismuth.

nitric and hot sulphuric acids. Its symbol, Hg, is from the Latin *hydrargyrum*. It is used in making thermometers, barometers, and other physical instruments, in silvering mirrors, in the manufacture of many medicinal preparations, and in extracting gold and silver from their ores. With many of the metals it unites easily, forming a class of alloys called *amalgams*. In handling mercury great care should be taken to prevent it from coming in contact with gold rings or other jewelry, on account of the readiness with which gold amalgamates. A bit of gold-leaf will dissolve in a drop of quicksilver almost instantaneously (see Experiment 100).

Mercury forms two sets of compounds, which are called *mercurous* and *mercuric* compounds respectively. In the first set, which are unstable, it seems to be a monad; in the second it is unmistakably bivalent. The following are its more important compounds:

Mercur*ic* oxide, HgO, is the well-known red oxide formed by heating mercury in the air. At a temperature above 350° it gives off its oxygen, and is noted as the substance from which that gas was first obtained pure (see Experiment 2, and Chapter IV). Mercur*ous* oxide, Hg_2O, is black and unstable. Mercuric sulphide, HgS, has already been referred to as the ore cinnabar. When H_2S is passed into a solution of a mercuric salt, the same sulphide is thrown down as a black precipitate. By subliming a mixture of mercury and sulphur it is obtained in a bright-red modification, called vermilion, which is used as a scarlet pigment.

When mercury is treated with nitric acid in quantity insufficient to dissolve the whole of it, mercurous nitrate, $HgNO_3$, is produced in white crystals. With an excess of nitric acid the mercuric salt, $Hg(NO_3)_2$, is formed. With hot sulphuric acid mercury yields mercuric sulphate, $HgSO_4$; a compound used in some forms of galvanic battery.

The chlorides of mercury, $HgCl$* and $HgCl_2$, are both important. Mercurous chloride is a white, insoluble powder, much used in medicine under the familiar name of *calomel.* Mercuric chloride, which is prepared on a large scale by subliming a mixture of mercuric sulphate and common salt, is soluble in water, alcohol, and ether, and crystallizes easily. It is the well-known violent poison, *corrosive sublimate.* The best antidote for this poison is white of egg, administered raw, in large doses. The albumen of the egg forms an insoluble clot with the mercuric chloride, which may afterward be removed from the stomach by means of an emetic.

Both of the mercury iodides are employed medicinally. The mercurous compound is green; the mercuric salt is bright scarlet. The properties of the latter substance are so extraordinary that, although they were partly brought out in Experiment 3, they deserve further experimental attention here.

EXPERIMENT 86.—Dissolve in water, in separate vessels, nine parts of mercuric chloride and eleven of potassium iodide. Mix the two colorless solutions, and a heavy precipitate, yellow at first, scarlet afterward, will form. Shake vigorously and divide into

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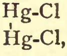
* Many chemists write this Hg_2Cl_2, or  $\begin{matrix}\text{Hg-Cl}\\ | \\ \text{Hg-Cl}\end{matrix}$, regarding mercury as invariably dyad. Good arguments can be cited in favor of either formula.

three portions. To one portion add an excess of mercuric chloride solution, and to the second portion an excess of potassium iodide. In each case the precipitate will redissolve, leaving the fluid colorless. Filter the third portion, and wash and dry the precipitate. Heat a little of it gently on a bit of porcelain or a slip of glass, and it will change from scarlet to bright yellow. On cooling, it will pass slowly back to its original color. Under the microscope this change is very beautiful, inasmuch as the scarlet may be seen to leap from particle to particle of the yellow powder.

These color-changes are due to the fact that mercuric iodide exists in two distinct modifications, having different optical properties and different crystalline form. In Experiment 3 we have an example of *dry* double decomposition, which is one of the very rarest of chemical phenomena.

CHAPTER XXV.

THE ALUMINUM GROUP.

ALUMINUM, as regards abundance, may be ranked side by side with sodium, calcium, and magnesium. It enters into the composition of all the important primitive rocks, and all slates and clays consist mainly of its silicates. In the crust of the earth, only oxygen and silicon occur in larger quantities.

The metal itself is prepared by passing the vapor of a double chloride of aluminum and sodium over metallic sodium. Sodium chloride is formed, and metallic aluminum is set free.* It is a tin-white metal, brilliant, malleable, and ductile, and has a specific gravity of 2.583. It fuses at about 850°, and is an excellent conductor of heat and electricity. It does not tarnish in the air, it is easily worked, and it combines the properties of lightness and strength to an extraordinary degree. If it could only be produced cheaply from common clay, it would be one of the most useful of metals. Indeed, it has been called "the metal of the future," although at present it is only employed for a very few purposes. An alloy of ten parts of aluminum

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* Several modified processes for the manufacture of aluminum have recently been patented in England.

with ninety of copper is known as aluminum bronze, and is a dangerous imitation of gold. It is somewhat used in fine philosophical instruments.

Aluminum is trivalent, and has an atomic weight of 27. It forms one set of compounds, of which the oxide, alumina, Al_2O_3, is the type. Such oxides as Al_2O_3, Fe_2O_3, Cr_2O_3, and Mn_2O_3, are termed *sesquioxides*.

Alumina occurs crystallized in nature as the mineral corundum, and is usually colored by impurities. The yellow variety is called "Oriental topaz"; the purple is the "Oriental amethyst"; the green is the "Oriental emerald." The sapphire is merely blue corundum, and the ruby is a red variety. These gems can now be produced artificially. Emery, which is so important as a polishing-powder, is an impure corundum.

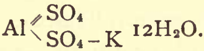
Aluminum forms several hydroxides, the compound $Al_2(OH)_6$ being the most characteristic. When artificially precipitated, as by the addition of ammonia to an aluminum salt, they possess the property of uniting with organic dye-stuffs to form insoluble substances called "lakes." Aluminum hydroxide, therefore, plays an important part in the processes of dyeing, being thrown down in the fiber of the cloth for the purpose of fixing and retaining colors.

EXPERIMENT 87.—Dissolve a crystal of alum in water, and add ammonia to the solution. Warm, and filter off the insoluble, gelatinous $Al_2(OH)_6$ which is precipitated. Now pour over the precipitate a solution of logwood or cochineal. The color will be retained and can not be washed out.

In alumina we have an oxide which may play the part of either an acid-former or a base. With strong acids it forms characteristic salts, like the sulphate; and with strong bases it unites to produce aluminates.

EXPERIMENT 88.—To a solution of alum add a very little caustic potash or caustic soda. A precipitate of hydroxide will be thrown down, which will be redissolved upon the addition of more alkali. Metallic aluminum itself may be dissolved, with evolution of hydrogen, by potassium or sodium hydroxide. In these reactions potassium or sodium aluminate is formed.

The most important simple salt of aluminum is the sulphate, $Al_2(SO_4)_3$, $18H_2O$. It is much used by dyers as a mordant; and an impure variety of it occurs in commerce under the name of alum-cake. It combines with the sulphates of the alkaline metals to form a class of double salts known as *alums*, of which potassium alum, K_2SO_4, $Al_2(SO_4)_3$, $24H_2O$, is the commonest example. The formula of this salt may be halved, and written $KAl(SO_4)_2$, $12H_2O$; or, structurally—



$$\mathrm{Al}\begin{matrix}\diagup \mathrm{SO_4} \\ \diagdown \mathrm{SO_4-K}\end{matrix}\ 12\mathrm{H_2O}.$$

With ammonium sulphate, ammonium alum is formed; and so also we may put either Na, Ag, Tl, Cs, or Rb in place of K, or Cr, Ga, In, Fe, or Mn in place of Al. In every case we shall have a salt containing twelve molecules of water, and crystallizing in regular octahedra; and all of these salts may be represented by the general formula—

$$M^{i}M^{iii}(SO_4)_2,\ 12H_2O,$$

in which M^{i} stands for a univalent metal and M^{iii} for a triad. The potassium and ammonium aluminum alums are both important, and are used as mordants in the art of dyeing.

In the mineral kingdom, in addition to the species already mentioned, we find a number of highly interesting aluminum compounds. The turquoise is an aluminum phosphate, the garnet and emerald are silicates containing aluminum, and the topaz is a compound which may be represented by the formula $Al_2SiO_4F_2$. Another substance of special interest is cryolite, a double fluoride of aluminum and sodium, $6NaF, Al_2F_6$, which forms a vast bed in Western Greenland.* Thousands of tons of this mineral are annually brought to the United States, and worked over by a special process so as to yield aluminum sulphate and an excellent quality of soda-ash. A kind of glass which outwardly resembles porcelain is also made by fusing cryolite with sand.

A beautiful blue ornamental stone, lapis lazuli, is a silicate of aluminum and sodium containing sulphur. Formerly its powder was used by artists as a paint, under the name of ultramarine; but at present this substance is produced artificially from very cheap materials. First, a mixture of clay with sodium sulphate, soda, charcoal, and sulphur, is heated in crucibles, and a valuable paint known as green ultramarine is obtained. This, reheated with sulphur, yields blue ultramarine, which is much used for water-colors and for paper-staining. In 1829 ultramarine was worth, in England, sixty dollars a pound; to-day its price is about twelve cents. Nearly twenty million pounds are annually made. Violet and red ultramarines have also been pre-

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* Cryolite has recently been discovered near Pike's Peak, in Colorado.

pared; but to none of these compounds can absolutely definite chemical formulæ as yet be assigned.

Pottery and porcelain, being made from clay, are more or less impure silicates of aluminum. Red bricks and red pottery owe their color to compounds of iron; and fire-clay, from which the fire-brick linings of furnaces are made, contains large admixtures of silica. Porcelain differs from glass in being non-transparent, or at best only translucent, and exceedingly infusible.

Pure porcelain-clay or kaolin is a hydrous aluminum silicate, $H_2Al_2Si_2O_8 + H_2O$. It is derived from rocks containing feldspar ($K_2Al_2Si_6O_{16}$), by the atmospheric process known as weathering. When it is baked in an appropriate furnace, it loses water and hardens, and a porous mass is produced. In making porcelain the finely-powdered kaolin is mixed with water to a very thick paste, and then molded into the desired shape. A little feldspar, chalk, or gypsum is also added to the clay, in order to form a fusible silicate in quantity just sufficient to bind the particles of the ware firmly together. Upon firing, as the process of burning is called, a porous "biscuit-ware" is obtained, which is afterward subjected to a process of glazing. For the finest porcelain the glazing material is generally pure feldspar, finely powdered and mixed with water to a very thin consistency; into this the biscuit is dipped, and then fired over again. The feldspar, being fusible, melts; and a thin, smooth, glassy layer covers the surface of the ware. A cheaper glaze for common stone-china consists of a mixture of clay, chalk, ground flints, and borax; but many other recipes are also used. Earthenware is generally salt-glazed, a process which consists in throwing common salt into the kiln just before the firing is finished. The salt volatilizes, and a fusible silicate of aluminum and sodium is formed all over the surface of the pottery. The colors used in decorating porcelain consist of various metallic oxides; cobalt oxide for blue, chromic oxide for green, etc. Some colors are put on previous to glazing; but the more delicate tints, as well as any gilding, are imparted in a separate firing over the glaze.

GALLIUM, which is chemically allied to aluminum, is an excessively rare metal, of atomic weight 69. It was discovered in 1875, and is interesting as being one of the metals of which the existence and properties were predicted in advance of actual discovery. Its specific gravity is 5.9, and it melts at 30° C. It becomes liquid in the heat of the hand! Its oxide is Ga_2O_3, and its sulphate forms alums.

INDIUM, atomic weight 113.5, was discovered in 1875. Like gallium, it is exceedingly rare. The metal has a specific gravity of 7.4, and outwardly resembles zinc. Its sulphate forms an alum. Indium and gallium were both discovered by spectrum analysis, and both are trivalent.

Scandium, yttrium, terbium, erbium, and ytterbium are very rare metals having only theoretical interest. They are all trivalent, forming sesquioxides, which are strong bases. The existence of scandium was predicted by Mendelejeff in advance of its actual discovery by Nilson.

Cerium, lanthanum, and didymium are three other rare metals which usually occur associated together. Lanthanum is a triad, cerium a tetrad, and didymium a pentad. With didymium, in intimate admixture, a fourth metal, samarium, has recently been detected. Cerium oxalate has a limited use in medicine.

CHAPTER XXVI.

THE TETRAD METALS.

IN addition to cerium, which was mentioned in the preceding chapter, titanium, zirconium, tin, lead, and thorium are quadrivalent. In fact, they may all be classed in a series of elements of which carbon and silicon are the first and second members. TITANIUM, atomic weight 50, is one of the rarer metals. Its oxide, TiO_2, is a natural mineral, and has a limited application in giving a yellowish tint to porcelain. Titanium occurs in many iron-ores, and renders them more difficult of working. In the blast-furnace it sometimes combines with nitrogen and carbon so as to form a nitrocyanide, $Ti(CN)_2 + 3Ti_3N_2$, which looks strikingly like metallic copper. ZIRCONIUM, atomic weight 90, is even rarer than titanium. Like alumina, zirconia (ZrO_2) is sometimes basic and sometimes acid-forming. The mineral zircon, $ZrSiO_4$, is used, under the name of *hyacinth*, as a gem. THORIUM, atomic weight 232, is exceedingly rare, and has no practical importance. Its oxide is a strong base.

TIN, atomic weight 118, is rarely found in the metallic state, and occurs in only a few mineral species. It has but one important ore, the mineral cassiterite or tin-stone, SnO_2. This ore varies in color from brown to black, and is quite heavy; but it is devoid of metallic luster, and might easily be passed over as valueless by an untrained observer. Tin is the only valuable metal which has not as yet been found in paying quantities within the limits of the United States. It is chiefly produced in Cornwall, Borneo, Malacca, and the Island of Banca. Banca tin is almost chemically pure, while English tin always contains a little iron and lead.

Tin is easily extracted from its ore by heating the crushed mineral with coal or charcoal in a reverberatory furnace.

$$SnO_2 + C = Sn + CO_2.$$

It is a white metal, of specific gravity 7.3, and a melting-point of 235°. Melted tin readily absorbs oxygen from the air, and becomes converted into a white oxide, SnO_2. When a bar of tin is bent, it emits a peculiar crackling sound, called the "tin-cry," which is caused by the friction against each other of interlaced crystals. The crystalline character of the metal may be rendered evident to the eye by washing the surface of a piece of tin-plate with warm dilute nitro-hydrochloric acid. Crystalline markings will presently appear. Tin is ductile, but not tenacious; it is also highly malleable, and is therefore much used in the form of foil. The cheaper grades of tin-foil are adulterated with lead.

Tin-plate, or sheet-tin, is really tinned iron. Sheets of rolled iron, chemically clean, are dipped into melted tin, and acquire a coating of the latter. Ordinary mirrors are covered with an amalgam of tin and mercury; bronze is an alloy of copper and tin; plumber's solder consists of tin and lead, and Britannia-metal is composed mainly of tin and antimony.

The symbol of tin, Sn, is from the Latin *stannum.* There are two sets of tin compounds, which are termed stannous and stannic compounds respectively. Stannous oxide, or tin monoxide, SnO, is basic, and from it a well-defined series of salts may be derived. Stannic oxide, or tin dioxide, SnO_2, is weakly basic with strong acids, and weakly acid with strong bases. Sodium stannate, $Na_2SnO_3, 3H_2O$, is an important mordant in calico-printing. Stannous chloride, $SnCl_2, 2H_2O$, and stannic chloride, $SnCl_4, 5H_2O$, are also much used as mordants. The anhydrous stannic chloride, $SnCl_4$, is a volatile liquid; but its hydrate is a crystalline salt. Stannic sulphide, SnS_2, forms golden scales which are used for bronzing plaster casts. Its commercial name is "mosaic gold." The close analogy between tin and other members of the same group is shown by the subjoined formulæ:

CO	——	TiO	SnO
CO_2	SiO_2	TiO_2	SnO_2
CCl_4	$SiCl_4$	$TiCl_4$	$SnCl_4$
Na_2CO_3	Na_2SiO_3	Na_2TiO_3	Na_2SnO_3

LEAD, although classed with the tetrads, is in most of its compounds bivalent, and might fairly be put in the same group with calcium and barium. In chemical structure its commoner salts resemble those of the latter metals; but in certain organic compounds it is unmistakably quadrivalent.

The carbonate, sulphate, phosphate, and arsenate of lead all occur in nature as well-defined, crystallized, mineral species; but the only ore of lead having much practical importance is the sulphide, PbS, which is commonly known as galena. This ore is easily reduced by heating in a reverberatory furnace, as follows: First, it is roasted with free access of air, when a portion is oxidized to a sulphate, $PbSO_4$, and another to oxide, PbO, while a third part remains unchanged. At the proper time the air is excluded and the temperature is raised; sulphur dioxide is given off, and lead is left behind, in accordance with the subjoined equations. Both reactions occur simultaneously:

$$PbSO_4 + PbS = 2Pb + 2SO_2.$$
$$2PbO + PbS = 3Pb + SO_2.$$

In actual working a little lime is added in order to form a fusible slag with the impurities of the ore. In many cases the lead contains some silver, which is afterward extracted by the process described in the chapter upon that metal.

Lead is a bluish-white metal, of atomic weight 207, and specific gravity 11.38. It melts at 332°, and at ordinary temperatures is soft enough to be scratched by the finger-nail. When freshly cut it has a brilliant metallic luster; but it quickly tarnishes on the surface and becomes dull. It is malleable and ductile, but its tenacity is so slight that it is not available for wire or for very thin foil. The symbol, Pb, is from the Latin *plumbum*.

The salts of lead are all poisonous; and hence it is often an important matter to determine whether or not leaden water-pipes affect drinking-water injuriously. Even the slightest traces of lead, taken day by day into the system, will in time accumulate so as to cause very serious illness. Perfectly pure water, free from air, does not attack lead; but water containing air corrodes it slowly. Drinking-waters all contain salts in solution, and these vary with different localities and different sources of supply. Hard water, or water carrying either sulphates or carbonates dissolved in it, soon forms a thin, insoluble coating on the surface of lead pipe, and protects it from further action. Such waters, therefore, are relatively safe. On the other hand, water containing nitrates, chlorides, or free carbonic acid, will gradually take lead into solution, and consequently may become unwholesome by contact with that metal. In using lead pipes the safest rule is never to drink water which has been long standing in them. Always allow the water to run until it flows relatively fresh from the cistern or water-mains. If water is suspected of containing lead, the impurity may be detected by adding a few drops of hydrochloric acid and passing into it a current of sulphuretted hydrogen. If lead is present, a brownish tinge will be produced, which may best be observed by looking through a very thick layer of the liquid. With much lead in a solution, sulphuretted hydrogen yields a heavy black precipitate.

Lead forms a number of important compounds, in most of which it plays the part of a dyad. For example, there are the sulphate, $PbSO_4$; a nitrate, $Pb(NO_3)_2$; a chloride, $PbCl_2$, etc. The acetate, or sugar of lead, will be described under acetic acid, and the chromate, chrome-yellow, belongs in the chapter with chromium. With oxygen lead combines in three proportions, forming a monoxide,

PbO; a dioxide, PbO_2, and the compound known as red-lead or minium, Pb_3O_4. The last may be regarded as a double oxide, $2PbO + PbO_2$.

Lead monoxide, or litharge, is a yellowish powder which is formed whenever lead is heated with free access of air. It is a strong base, and combines freely with most acids. It is very largely used as an ingredient of flint-glass, which contains a colorless lead silicate; it is also employed in glazing earthenware, in preparing other lead compounds, and in medicine. The dioxide is a dark-brown powder having powerful oxidizing properties. Red-lead is made by heating litharge for several hours to dull redness, and forms a valuable paint. It is also used by the glass-makers, and in the preparation of some cements.

One of the most important compounds of lead is the basic carbonate, $2PbCO_3, Pb(OH)_2$, which constitutes the valuable paint known as white-lead. This may be prepared by several processes, the old "Dutch method" being the best. Spiral coils of sheet-lead are put in earthen pots with a little vinegar, and exposed for several weeks to the slow action of carbon dioxide generated by the fermentation of spent tan-bark or sawdust. First, a layer of the bark is put down, and on this the earthen pots are arranged in rows, covered with boards. On these another layer of bark is spread, then a second series of pots, and so on until many successive layers are arranged. The entire pile is finally covered with spent tan. After the proper lapse of time the lead is found to be converted into white-lead, which is thoroughly washed, dried, and ground up with linseed-oil. It is often adulterated with barium sulphate.

Although white-lead is by far the most brilliant of the white paints, it is subject to some objections. It is readily blackened by sulphuretted hydrogen, and it is poisonous to the workmen who handle it. House-painters are often subject to the painful disease known as lead-colic, which is caused by the slow absorption of small particles of white-lead into the system. Baryta-white and zinc-white are less beautiful than white-lead, but they do not blacken and they are not unwholesome.

From solutions containing lead the metal is easily thrown down.

Experiment 89.—Suspend a rod or strip of zinc in a solution of lead acetate. In the course of a few hours the zinc will be covered with brilliant metallic spangles of lead, forming what is called the "lead-tree." For every atom of lead thrown down, one atom of zinc goes into solution. If the process be continued long enough, all the lead will separate out, and zinc acetate will remain dissolved:

$$Pb(C_2H_3O_2)_2 + Zn = Zn(C_2H_3O_2)_2 + Pb.$$

Similarly, metallic mercury, placed in a solution of silver nitrate, will precipitate metallic silver, and be itself dissolved; copper will precipitate mercury; iron or zinc will throw down copper, and so on. With each pair of metals the one which is precipitated is electro-negative to the one which displaces it from solution. The more electro-positive a metal is, the stronger will be its affinity for acids.

CHAPTER XXVII.

THE ANTIMONY GROUP.

In the same natural group of elements with nitrogen, phosphorus, and arsenic, we find the metals vanadium, antimony, and bismuth. Each of these substances, like phosphorus, may act either as a triad or a pentad, and each is clearly related to the others through a regular gradation of properties. This is indicated in the following table of atomic weights, specific gravity, and formulæ:

	Atomic weight.	Specific gravity.				
Nitrogen	14	——	N_2O_3	N_2O_5	HNO_3	——
Phosphorus	31	1.837	P_2O_3	P_2O_5	HPO_3	H_3PO_4
Vanadium.......	51.5	5.500	V_2O_3	V_2O_5	HVO_3	H_3VO_4
Arsenic	75	5.700	As_2O_3	As_2O_5	——	H_3AsO_4
Antimony	120	6.702	Sb_2O_3	Sb_2O_5	$HSbO_3$	——
Bismuth	208	9.823	Bi_2O_3	Bi_2O_5	$HBiO_3$	——

If we consider the series of compounds beginning with nitric acid, we shall find that what may be called the chemical intensity decreases as we ascend. Nitric acid is a very strong acid; phosphoric acid is a little weaker; and so on, until we reach bismuthic acid, $HBiO_3$, which is exceedingly feeble. In general, bismuth is a basic metal, and antimony may act either as an acid-former or as a base.

VANADIUM, although traces of it occur widely diffused in many rocks, is one of the very rare metals. Until quite recently its compounds had no practical applications whatever, but now they are rapidly coming into use for the preparation of a very fine black ink, and in dyeing with aniline black. Vanadic acid behaves like arsenic and phosphoric acids, and forms a similar variety of salts. Like nitrogen, vanadium forms five oxides—V_2O, VO, V_2O_3, VO_2, and V_2O_5.

ANTIMONY, although not widely diffused, is nevertheless quite abundant in some localities, and ranks commercially as one of the cheaper metals. It is found as native antimony, as sulphide, Sb_2S_3, as oxides, and in a variety of other mineral species. Some of the more important silver-ores are double sulphides containing antimony.

The metal is easily obtained from its sulphide by heating the latter with scrap-iron. It melts at 450° C., and at a red heat is volatile. The vapor oxidizes easily in the air, and forms dense white clouds of Sb_2O_3. In color, antimony is bluish white, and in texture it is highly crystalline. It is so brittle that it may readily be pulverized in a mortar. An allotropic variety of it, which is obtained by electrolysis, is curiously explosive when either scratched or heated. The symbol, Sb, is from *stibium.* Metallic zinc precipitates antimony from its solutions as a black powder, which, under the name of antimony black, is used for giving to plaster casts the appearance of steel.

Antimony is chiefly useful in its alloys. Type-metal is an alloy of antimony, lead, and tin, in proportions which vary with different makers. In solidifying from the fused state, type-metal expands, insuring an accurate copy of the type-mold. Lead, alone, contracts, and can not give sharp castings. The tin toughens the alloy, the antimony imparts the necessary hardness. Britannia-metal has already been referred to as composed of antimony and tin; and Babbit's anti-friction metal, which is used by machinists, contains antimony, lead, tin, and a little copper.

Antimony hydride, or antimoniuretted hydrogen, SbH_3, is a colorless gas resembling the corresponding arsenic compound. Its properties were sufficiently indicated under Experiment 77, and its formation affords a means of detecting antimony in analysis.

With oxygen, antimony forms three oxides—Sb_2O_3, Sb_2O_4, and Sb_2O_5. From the trioxide, by union with water, ortho-antimonious acid, H_3SbO_3, and meta-antimonious acid, $HSbO_2$, are derived; and in a similar way the pentoxide yields antimonic acid, $HSbO_3$. These acids are very weak, and their salts are unimportant. There are still other salts in which antimony is basic; and one compound of this kind, a tartrate of potassium and antimony, is used in medicine under the name of tartar emetic. The chlorides of antimony, $SbCl_3$ and $SbCl_5$, are easily formed by the direct union of the metal with chlorine. The first is a pasty solid, sometimes called "butter of antimony"; the second is liquid and volatile.

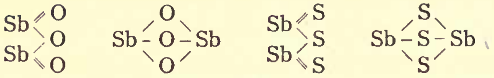
The sulphides of antimony, Sb_2S_3 and Sb_2S_5, are both interesting. Like the similar compounds of arsenic, they form sulpho-salts; thus:

$Na_2S + Sb_2S_3 = 2NaSbS_2$, sodium sulphantimonite.
$3Na_2S + Sb_2S_5 = 2Na_3SbS_4$, " sulphantimonate.

The trisulphide is the important ore of antimony, stibnite, a heavy gray mineral of brilliant metallic luster. In powder this mineral is an important ingredient of some fire-work mixtures. There is also an orange-colored modification of the same sulphide, which is easily obtained in the laboratory, thus:

EXPERIMENT 90.—Dissolve some powdered antimony in *aqua regia* ($HNO_3 + HCl$), and dilute the solution with water until it just begins to turn turbid. Divide it into two parts, and saturate one with a stream of hydrogen sulphide. Filter off the orange-red precipitate, dry it, and heat gently in a glass tube. It will be slowly transformed into the black modification, thus showing the relation between the two. To the second part of the solution add ammonium sulphide. The orange-colored precipitate will at first form, and then, upon the addition of more ammonium sulphide, will redissolve; this action being due to the production of ammonium sulphantimonite, which is soluble. Similar experiments may be performed with a solution of tartar emetic instead of the antimony solution above described. Nitric acid alone will convert antimony into a white oxide, which is insoluble.

The difference between the two varieties of antimony sulphide is probably due to a different arrangement of atoms in the molecule. The trioxide is also dimorphous, and the dimorphism in each case may be rendered clear by the subjoined structural formulæ, in which antimony is trivalent:



A red paint, antimony cinnabar, is a double compound of antimonious oxide and sulphide. Glass of antimony, which is used for imparting a yellow tint to glass and porcelain, is a substance produced by fusing together the oxide and the sulphide.

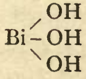
BISMUTH is less abundant than antimony, and is found in comparatively few minerals. The oxide and sulphide occur as definite natural species, but the metal itself is also found in nature, and furnishes the chief supply of bismuth to commerce. It is simply melted out from the adherent rocky material, and collected directly in the metallic state.

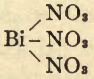
Bismuth is brilliant, brittle, and reddish white. It melts at 264° C., and on solidifying from fusion it expands, increasing about $\frac{1}{32}$ in volume. It crystallizes easily, and this fact has already been indicated in Experiment 65. The crystals are rhombohedral, but might readily be mistaken for cubes, and often display brilliant iridescent colors on the surface.

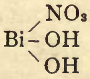
Bismuth is useful mainly in its alloys and its compounds. Its alloys are remarkable for their low fusibility, and several of them melt below the boiling-point of water. Rose's alloy consists of one part lead, one part tin, and two parts bismuth, and melts at 93.7° C. Wood's alloy, which melts at 60.5°, contains four parts bismuth, two of lead, one of tin, and one of cadmium. These alloys expand remarkably in solidifying from fusion, and are used in making casts of medals and coins. A plaster cast is first made, and then filled with the fusible alloy, which, expanding, fills and reproduces every line. Other alloys of this kind serve to make safety-plugs for steam-boilers. When the boiler gets too hot, the plug melts and the steam escapes harmlessly.

In its commoner compounds bismuth may be regarded as trivalent; and in most of its salts it acts distinctly as a base. Thus we have an oxide, Bi_2O_3, a chloride, $BiCl_3$, etc.; and such salts as the nitrate, $Bi(NO_3)_3$, and the sulphate, $Bi_2(SO_4)_3$. When water is added in large quantity to a solution of a bismuth salt, the latter is decomposed, and a basic compound is precipitated. The reaction is exceedingly characteristic, and is applied analytically to the detection of bismuth.

EXPERIMENT 91.—Dissolve some powdered bismuth in a little nitric acid, and divide the solution into two parts. Leave one to crystallize, and add a considerable quantity of water to the other. The first portion will yield crystals of bismuth nitrate, $Bi(NO_3)_3, 3H_2O$; and the second will form a copious white precipitate of the basic nitrate or subnitrate, $Bi(OH)_2NO_3$. The relation of these compounds to each other and to bismuth hydroxide may be rendered clear by formulæ, thus:







The basic nitrate is a very important medicinal agent in the treatment of bowel disorders. If water be added to the chloride of bismuth, $BiCl_3$, a similar white precipitate will be formed consisting of bismuth oxychloride, BiOCl. This compound has been used as a white face-powder, but is decidedly unwholesome. With sulphuretted hydrogen, bismuth solutions yield a black precipitate of bismuth sulphide, Bi_2S_3. The same compound is thrown down by ammonium sulphide, and is insoluble in an excess of the reagent.

Two other very rare metals, being pentads, properly belong in this chapter. They are columbium,* atomic weight 94, and tantalum, atomic weight 182. Their chlorides, $CbCl_5$ and $TaCl_5$, and their oxides, Cb^2O_5 and Ta_2O_5, are characteristic compounds. From the oxides, columbic and tantalic acids are derived, and salts of these acids exist in a few rare minerals.

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* Also known as niobium. The name columbium has priority.

CHAPTER XXVIII.

THE CHROMIUM GROUP.

JUST as the metals of the preceding group are classed with nitrogen and phosphorus, so the metals of this group, chromium, molybdenum, tungsten, and uranium, may be regarded as members of the same elementary series with oxygen and sulphur. As metals they have little importance; but in many of their compounds they are very useful.

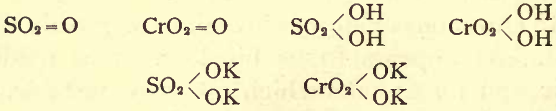
CHROMIUM, atomic weight 52, owes its name to a Greek word signifying *color*, and several of its compounds are important paints. It occurs in various minerals, but not very abundantly; its chief ore being chromite, $FeCr_2O_4$. The metal itself is obtained with great difficulty, is almost absolutely infusible, and has a specific gravity of 6.81. It forms several distinct sets of compounds.

In chromous oxide, or chromium monoxide, CrO, chromium appears to be bivalent. This oxide is basic, and forms salts which are very unstable, and rapidly absorb oxygen from the air.

Chromic oxide or chromium sesquioxide, Cr_2O_3, is the most stable of the chromium compounds. It is a brilliant-green powder, which is used in giving a green color to glass and porcelain. The emerald owes its hue to traces of this compound. From it as a base many salts may be derived; for example, there is a sulphate $Cr_2(SO_4)_3$, a chloride, Cr_2Cl_6, etc. The chloride forms superb violet-colored scales. Like aluminum sulphate, chromic sulphate forms alums, of which common chrome alum, $KCr(SO_4)_2, 12H_2O$, is the type. This may be obtained in violet-colored octahedral crystals as follows:

EXPERIMENT 92.—Dissolve about thirty grammes of potassium pyrochromate * in the smallest possible quantity of water, add forty grammes of sulphuric acid, largely diluted, and boil with successive additions of small quantities of alcohol until the original orange color of the solution is completely changed to green. Upon moderately long standing, crystals of chrome alum will be deposited. The reaction involves the reduction of the highly oxidized chromate to the lower oxidation of the chromic salt. At the same time, the alcohol, which serves as the reducing agent, is itself oxidized.

Chromium trioxide, CrO_3, is the starting-point from which chromic acid, H_2CrO_4, and a large number of chromates may be derived. These chromates and the trioxide resemble the sulphates and sulphur trioxide in chemical structure: †



$$SO_2=O \qquad CrO_2=O \qquad SO_2{<}\begin{matrix}OH\\OH\end{matrix} \qquad CrO_2{<}\begin{matrix}OH\\OH\end{matrix}$$

$$SO_2{<}\begin{matrix}OK\\OK\end{matrix} \qquad CrO_2{<}\begin{matrix}OK\\OK\end{matrix}$$

Chromium trioxide is easily obtained from any chromate by treatment with sulphuric acid; thus:

EXPERIMENT 93.—Add strong sulphuric acid,

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* Commonly called bichromate of potash.

† Refer to Chapter XVI.

very gradually, to a strong solution of potassium pyrochromate. Heat will be evolved; and, upon cooling, superb crimson needles of the trioxide will be deposited. These may be dried by draining on a porous brick or tile, but should not be brought in contact with any organic matter. Most organic bodies are oxidized by them, Cr_2O_3 being simultaneously formed. In Experiment 92 a reaction of this kind took place, which may be further illustrated by dropping strong alcohol upon the dry trioxide. The alcohol will be ignited by the heat of the oxidation. The aqueous solution of chromium trioxide is yellow, and may be regarded as containing chromic acid, H_2CrO_4,

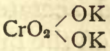
$$(H_2O + CrO_3 = H_2CrO_4).$$

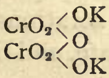
Nearly all of the chromates are either red, orange, or yellow, and several of them are exceedingly important.

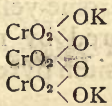
Potassium forms three chromates; the first one, K_2CrO_4, being the normal salt. The other two may be represented as formed from this by the addition of one and two molecules of CrO_3 respectively, as follow:

$K_2CrO_4 + CrO_3 = K_2Cr_2O_7$, potassium pyrochromate.
$K_2CrO_4 + 2CrO_3 = K_2Cr_3O_{10}$, " trichromate.

Structurally, the three salts may be represented thus:







The second of these chromates, the dichromate or pyrochromate, is by far the most important of all the compounds of chromium, and from it the others are prepared. It is made directly from chromite (chrome iron-ore) by roasting the finely powdered mineral in a strong oxidizing flame with potassium carbonate and a little lime. Sometimes saltpeter is added also. The roasted mass yields with water a yellow solution of monochromate; which, treated with a quantity of sulphuric acid half sufficient to set its chromic acid free, deposits, on cooling, superb orange-red crystals of the desired salt.

Potassium pyrochromate is largely used in dyeing and calico-printing, in preparing the various chromium paints, as an oxidizing agent in bleaching discolored fats and oils, and in certain of the processes of photography. Paper dipped in a solution of it acquires a pale-yellow tint, but becomes brown on exposure to light.* A film of gelatine saturated with the salt becomes insoluble wherever it has been acted on by light, but remains soluble in its other portions. A photograph, therefore, taken on such a film, may be made to stand out in actual relief by simply dissolving away the unattacked parts; and then either copied in electrotype or in type-metal, or transferred to a lithographic stone. This fact is the basis of all the processes of photographic printing, such as are used in the production of heliotypes, autotypes, photo-lithographs, etc.†

Another important chromate is lead chromate, or chrome-yellow, $PbCrO_4$. This useful paint is prepared by mixing solutions of lead acetate and potassium pyrochromate, and filtering off the bright-

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* Repeat Experiment 83, using $K_2Cr_2O_7$ instead of $AgNO_3$. The print may be rendered permanent by thorough washing with water.

† For details, see Abney's "Treatise on Photography."

yellow precipitate.* Boiling with a caustic alkali converts it into chrome-red, $PbCrO_4, PbO$. Chrome-orange is a mixture of chrome-red and chrome-yellow.

MOLYBDENUM, atomic weight 96, is one of the rarer metals. Its chief ore is molybdenite, MoS_2, which strongly resembles graphite in its outward appearance. It forms complicated compounds, but its leading oxide, MoO_3, and molybdic acid, H_2MoO_4, are analogous to the corresponding oxides and acids of sulphur and chromium. Ammonium molybdate is a very important, practically indispensable reagent, in the exact analysis of iron-ores and fertilizers.

TUNGSTEN, atomic weight 184, is somewhat rare, though more abundant than molybdenum. It is found in several minerals, but chiefly in a tungstate of iron, wolfram, $FeWO_4$. The symbol, W, is derived from wolfram; but the name of the metal itself, of Swedish origin, signifies *a heavy stone*. Wolfram is a frequent and troublesome impurity among tin-ores, and miners regard it as a sign of tin.

Tungsten itself is a grayish metal, of specific gravity 19.26, being almost as heavy as gold. Its addition to steel in small quantities is said to give the latter superior hardness and fineness.

Like molybdenum, tungsten forms very complicated compounds. Some of them have great theoretical interest, but need no description here. Tungsten trioxide and tungstic acid, WO_3 and H_2WO_4, show its relations to the other metals of the group, and the hexchloride, WCl_6, indicates its sexivalency.

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* The experiment is a good and easy one for the pupil to try.

One of the tungstates of sodium is sometimes used as a mordant, and also for rendering cloth fabrics uninflammable.

URANIUM, atomic weight 239, is another of the rarer metals. When pure, it is silver-white, very difficultly fusible, and of specific gravity 18.685. It is found in a considerable number of minerals, but is generally obtained from pitchblende, an impure U_3O_8. This oxide is a compound of two others, UO_2 and UO_3; and still another, UO_4, has recently been discovered. The trioxide, UO_3, is a yellow powder; and from it a series of salts, similar in composition to the pyrochromates, are derived. The sodium and ammonium uranates, $Am_2U_2O_7$ and $Na_2U_2O_7$, both occur in commerce under the name of "uranium yellow," and are used in coloring glass and porcelain. The uranium glass has a peculiar greenish-yellow color (canary glass), and is highly fluorescent. In two other series of salts uranium is basic. The uranic nitrate and acetate are useful laboratory reagents.

Although uranium and its compounds have but limited importance, the metal itself affords a good illustration of the *law of Dulong and Petit.* This is a physical law of much value in the determination of atomic weights, and therefore it may be profitably considered here.

If two different substances, equal in weight, be exposed to the same source of heat, they will be found to gain in temperature with very unequal rapidity. A kilogramme of water, for example, requires about thirty times as much heat to raise its temperature one degree as is required to produce the same effect upon the same quantity of mercury.

Hence the *specific heat* of mercury is said to be one thirtieth of that of water. By the term *specific heat* we express the relative amounts of heat needed to raise equal weights of substances through equal ranges of temperature. Water has the highest specific heat of any substance known, and is taken as the standard of comparison or unity. The specific heat of other substances is expressed in fractions of unity. In other words, the quantity of heat necessary to raise the temperature of one kilogramme of water 1° C. is said to be one unit. The fraction of such a unit which is required to raise the temperature of a kilogramme of any other substance 1° C. is called its specific heat.

Now, the law of Dulong and Petit is based upon the fact that, when the specific heats of the metals are multiplied by their atomic weights, the products are sensibly equal. The product in each case is called the *atomic heat* of the metal; and the law which is deduced is as follows: *all the elementary atoms have equal capacities for heat.*[*] This is shown in the table, which includes some of the non-metals:

Table of Specific and Atomic Heat.

NAME.	Atomic weight.	Specific heat.	Atomic heat.	NAME.	Atomic weight.	Specific heat.	Atomic heat.
Aluminum . .	27.	.2253	6.08	Calcium	40.	.1686	6.74
Antimony. . .	120.	.0523	6.28	Cerium	141.	.0448	6.32
Arsenic.	75.	.0822	6.16	Cobalt	59.	.1062	6.26
Barium	137.	.05	6.85	Copper	63.3	.0951	6.00
Bismuth	208.	.0305	6.34	Didymium . .	145.	.0456	6.61
Cadmium . . .	112.	.0548	6.14	Gallium.	69.	.079	5.45

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[*] For fuller discussions of this law, see Wurtz's "Atomic Theory," and Chapter III of Remsen's "Theoretical Chemistry."

Table of Specific and Atomic Heat (continued).

NAME.	Atomic weight.	Specific heat.	Atomic heat.	NAME.	Atomic weight.	Specific heat.	Atomic heat.
Gold	196.5	.0316	6.18	Platinum....	195.	.0323	6.29
Indium......	113.5	.0565	6.61	Rhodium	104.?	.0580	6.03
Iridium......	193.	.0326	6.29	Ruthenium ..	104.?	.0611	6.35
Iron.........	56.	.1116	6.25	Selenium....	79.	.0860	6.79
Iodine......	127.	.0541	6.87	Silver........	108.	.0559	6.04
Lanthanum..	138.	.0418	6.18	Sodium	23.	.2934	6.75
Lead........	207.	.0315	6.52	Sulphur......	32.	.2026	6.48
Lithium......	7.	.9408	6.59	Tellurium...	125.	.0475	5.94
Magnesium..	24.	.2499	6.00	Thallium....	204.	.0325	6.63
Manganese..	55.	.1217	6.70	Thorium....	232.	.0279	6.47
Mercury	200.	.0333	6.66	Tin..........	118.	.0548	6.47
Molybdenum	96.	.0722	6.93	Tungsten....	184.	.0334	6.15
Nickel......	58.	.1075	6.23	Uranium	239.	.0275	6.56
Osmium......	199.?	.0311	6.19	Zinc.........	65.	.0939	6.09
Palladium...	106.	.0592	6.27	Zirconium...	90.	.0667	6.00
Phosphorus ..	31.	.202	6.26				

There are a few apparent exceptions to the law, but they need no notice here. The slight variations from exact equality in the column of atomic heats are due to unavoidable errors of experiment.

In the case of uranium there was until recently some doubt as to whether its atomic weight was 239; or only half as great; and the analyses of its compounds gave formulæ which agreed equally well with either value. Thus, in UO_3 we have 239 parts of uranium, combined with 48 of oxygen; while, if $U = 119.5$, we should write the formula U_2O_3, and express precisely the same ratio.* The uncertainty was at last dispelled by a determination of the specific heat of uranium, which Zimmermann found to be .028. This, multiplied by 239, gives a

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* The values 120 and 240 have commonly been given to U, but 119.5 and 239 are probably more nearly exact.

value for the atomic heat of 6.69, which agrees with the other metals; whereas 119.5 would have given a product very far too small. In many other cases the atomic weights of elements have been unsettled until the specific heats could be ascertained, and that value selected which agreed best with Dulong and Petit's law.

CHAPTER XXIX.

MANGANESE AND IRON.

MANGANESE, iron, nickel, and cobalt are so closely related that they may fairly be called the *iron group* of metals. They are near each other in metallic properties, and their compounds have very many points of similarity. In valency they range from two, to four, six, and eight.

MANGANESE is one of the commoner elements, and is very widely diffused. It occurs in many rocks and minerals, but its chief ores are pyrolusite, MnO_2, and manganite, Mn_2O_3, H_2O. The metal itself is somewhat difficult to prepare, and in appearance is similar to cast-iron. It oxidizes very easily, is slightly magnetic, very difficultly fusible, and has a specific gravity of 8.0. Its atomic weight is 55.

With oxygen, manganese combines to form the oxides MnO, Mn_2O_3, Mn_3O_4, MnO_2, and Mn_2O_7. From the monoxide, MnO, a series of manganese salts are derived, which are mostly rose-colored. Manganous sulphate, $MnSO_4, 5H_2O$, and manganous chloride, $MnCl_2, 4H_2O$, are the salts most often seen. In solutions of manganese compounds ammonium sulphide produces a flesh-colored precipitate of MnS. From Mn_2O_3, which is also a basic oxide, the manganic salts are prepared. Manganic sulphate,

$Mn_2(SO_4)_3$, unites with the alkaline sulphates to form alums; and in this particular manganese and chromium may be classed in one group with aluminum and iron. Most of the manganic salts are brown.

The oxides MnO_2 and Mn_3O_4 are neutral oxides; that is, they form neither acids nor bases. The first of these, commonly known as black oxide of manganese, occurs abundantly in many localities, and is simply ground up to powder and sent into commerce. Enormous quantities of it are used in making chlorine and bleaching-powder, in the preparation of oxygen, and as a material from which all the other compounds of manganese may be derived.

Manganese forms two acids: manganic acid, H_2MnO_4, known only in its salts, and permanganic acid, $HMnO_4$, which is derived from the oxide Mn_2O_7. $Mn_2O_7+H_2O=2HMnO_4$. Manganic acid belongs in the same class with sulphuric and chromic acids; while permanganic acid is similar in structure to perchloric acid. The salts $KClO_4$ and $KMnO_4$ are isomorphous. The manganates are green; the permanganates violet, red, or purple.

EXPERIMENT 94.—Mix a little MnO_2 with sodium carbonate, and fuse the mixture in the outer blow-pipe flame upon a slip of platinum foil. A green mass of sodium manganate will be formed, and by the production of this green color even the smallest traces of manganese may be detected. Dissolve the fused mass in cold water, and let the solution stand freely exposed to the air. It will slowly change color, passing from green through a series of intermediate tints, until at last it becomes a superb purple. These changes, which end in the production of sodium permanganate, caused the green mass to receive the popular name of "chameleon mineral."

Potassium permanganate, $KMnO_4$, is an important disinfectant. It forms nearly black crystals with a semi-metallic reflection from their surfaces, and it dissolves easily in water to an intense purple fluid. Even a trace of the salt will impart a rosy color to a large amount of water, and concentrated solutions of it are opaque. It is a powerful oxidizing agent, and is much used as a reagent in chemical analysis. Putrid water, or water which has acquired an unpleasant, woody taste, from long keeping in wooden cisterns or casks, may be rendered sweet by the addition of a very little potassium permanganate.

IRON, atomic weight 56, is the most familiar and useful of all metals, and one of the most abundant. It is contained in a vast number of minerals, in practically all rocks and soils, in the water of many springs, in plants, and in the red coloring-matter of blood. Occasionally it is found free in nature, and a considerable proportion of the meteoric masses which fall to the earth consist of metallic iron. One such mass from Brazil weighed 32,000 pounds.

But, although iron is so widely diffused, it is practically manufactured from only a very few ores. These are essentially the magnetic oxide, Fe_3O_4; hematite, Fe_2O_3; limonite, $2Fe_2O_3, 3H_2O$; and chalybite or spathic iron, $FeCO_3$. Of these, the magnetic ore is the richest, containing, when pure, 72.5 per cent of iron.

Pure iron is rarely seen. It is silvery white, softer than wrought-iron, almost infusible, and has a specific gravity of 7.8 to 8.0. It is extraordinarily malleable and ductile, and at the same time very tenacious; so that, even in the finest wire, it can support a considerable weight. The symbol, Fe, is from the Latin *ferrum.*

All commercial iron contains carbon, and its properties vary remarkably according to the proportion of the latter. Wrought-iron, or malleable iron, contains less than half a per cent of this impurity; cast-iron contains from two to six per cent, partly or wholly in chemical combination; steel is intermediate between the other two.

Wrought-iron is tough and fibrous in structure, and can be worked at a red heat by rolling or hammering. At the highest available temperatures it does not fuse, but merely becomes pasty; but, in this condition, two masses may be compactly hammered or *welded* together. This capability of welding is one of its most valuable properties. It is sometimes prepared directly from the ore, by heating the latter in a proper furnace with charcoal, and afterward purifying the pasty mass from adhering fuel and slag by thorough hammering. This process, which is known as *blooming*, has been in use from the remotest antiquity, and yields a remarkably fine quality of metal. It is, however, too expensive to be largely used at the present time; and to-day malleable iron is chiefly prepared by burning out the carbon from cast-iron. The latter, mixed with a certain amount of ferric oxide, is melted on the floor of a reverberatory furnace, and constantly stirred or shaken until it becomes pasty. The spongy lumps are then taken out, and worked into shape between heavy rollers. The whole process is technically known as *puddling*.

Cast-iron, which is a comparatively modern product, is made in the blast-furnace (Fig. 50). This consists of a tower from forty to ninety feet in height, having an interior diameter of from fourteen to seventeen feet in the maximum. Internally it is like two hollow cones placed base to base, and it is lined with the most refractory fire-brick. At the bottom, air is blown in by a powerful blast, through pipes which are called tuyeres;* and ac-

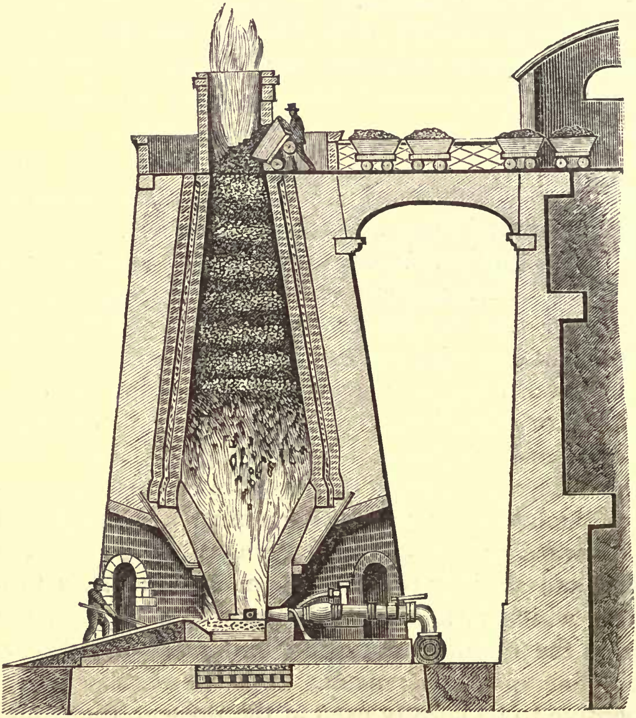

FIG. 50.—Section of Blast Furnace.

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* Pronounced "twyers."

cordingly, as hot or cold air is used, we have hot and cold blast-furnaces respectively. The hot-blast process is the more economical.

The furnace is fed at the top, and alternate layers of fuel, ore, and limestone are put in. The blast of air from the tuyeres furnishes oxygen, vivid combustion takes place, the oxides of iron are reduced by the carbon,* and the metal is set free. The latter dissolves some carbon, fuses, and settles to the bottom of the furnace, where it is drawn off from time to time into molds made of sand. The object of the limestone is to form an easily fusible slag with the silica of the ore, and with this slag many of the impurities are removed. When once kindled, a furnace should burn continuously for months, or even years; were the semi-fluid mass to solidify by too great a cooling, it would have to be dug out at great expense and at the cost of serious delay to the iron-master.

Cast-iron or pig-iron occurs in several forms, but is always crystalline in structure and more or less brittle. White cast-iron is very hard, highly crystalline, and quite brilliant. Gray cast-iron is softer and closer grained. Mottled iron is intermediate between the other two. In white iron, most of the carbon is combined chemically; in gray iron, a part has separated out in the form of fine scales of graphite. Spiegeleisen is a particularly brilliant white iron, containing about six per cent of carbon and some manganese. Common impurities in iron are silicon, sulphur, and phosphorus. The last two ele-

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* In reality, the chemical processes which take place in the blast-furnace are quite complicated. In them, carbon monoxide plays an important part.

ments are particularly objectionable, especially if the iron is to be either puddled or made into steel. Sulphur, in wrought-iron, renders the metal brittle when hot, or "hot-short"; the presence of phosphorus makes it brittle when cold, or "cold-short."

Steel may be made in several ways. Carbon may be added to malleable iron, or carbon may be withdrawn from cast-iron, or cast-iron and malleable iron may be melted together in the proportions needed to form a mixture having the composition and properties of steel. The last method is adopted in what is called the Siemens-Martin process. Of these methods, the first is by far the oldest. Bars of iron are packed in charcoal in tight boxes of fire-clay, and heated red-hot for a week or ten days. Carbon is slowly absorbed, and at the end of the operation the bars are found to have a curiously blistered appearance. By melting them in black-lead crucibles and casting them in ingots, *cast-steel* is obtained. The whole process is known as the cementation process, and cementation steel is considered the best for fine tools, knives, springs, etc.

The second process, by which carbon is taken away from cast-iron, was invented by Bessemer in 1856. In this process, about five tons of melted pig-iron are poured into an egg-shaped vessel called a "converter" (Fig. 51), through which a powerful blast of air can be blown. The converter is made of the strongest wrought-iron, and lined with an infusible layer of a silicious rock resembling fire-clay.* As the air bubbles through the molten iron, forced in from below, the temperature rises, carbon is

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* In the Gilchrist-Thomas process, which removes the phosphorus from the iron, the converter is given a "basic lining" of lime.

burned away, and the metal rapidly approaches the malleable state. Just before the latter is reached, however, a quantity of melted spiegeleisen is added, so as to supply just the amount of carbon needed for the production of good steel. The latter is then poured out into molds, and the operation is complete. By this process iron may be transformed into steel in less than half an hour, so that the saving of time in comparison with the cementation process is enormous. To-day, in consequence of Bessemer's invention, steel may be used for the manufacture of rails, car-axles, bridge-girders, boiler-plates, and cannon, and for a multitude of other purposes to which, thirty years ago, it was too expensive to be applicable. It is no exaggeration to say that the Bessemer process is revolutionizing the iron industry.*

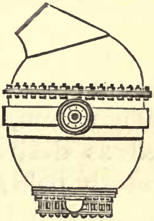

FIG. 51.—Bessemer Converter.

Steel owes its value to a variety of properties. Like cast-iron it is fusible, like wrought-iron it is malleable; it is capable of high polish, and may be rendered exceedingly hard. If heated to redness and suddenly quenched in cold water, it becomes both hard and brittle; but upon reheating and cooling slowly, it may again be rendered soft. By carefully regulating the heatings and coolings, intermediate degrees of hardness, brittleness, and elasticity may be attained; and by this process of "tempering," steel is adapted to a wide diversity of uses.

Like manganese and chromium, iron forms two

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* The best large treatise on the metallurgy of iron and steel is Percy's. A good summary of the subject is given in Roscoe and Schorlemmer's "Treatise on Chemistry," vol. ii, part ii, pp. 34–83.

distinct series of compounds, in which it plays the part of base. It also forms a very unstable series of salts, corresponding to ferric acid, H_2FeO_4, which are analogous to the chromates and manganates.

The ferrous salts, in which iron is apparently bivalent, are similar in structure to the salts of zinc, magnesium, and manganese. They may be regarded as derived from ferrous oxide, FeO, and are mostly pale green in color. By adding any caustic alkali, KOH, NaOH, or AmOH, to a solution of a ferrous hydroxide, $Fe(OH)_2$, is obtained as a greenish precipitate. Ferrous chloride, $FeCl_2, 4H_2O$, is easily prepared by dissolving iron in hydrochloric acid, and is used in some processes of metallurgy. Ferrous carbonate, $FeCO_3$, is a crystalline mineral, which, in a crude and impure state, is one of the most important ores of iron. Ferrous sulphide, FeS, is made by fusing iron and sulphur together in the proportion indicated by their atomic weights, and is employed in the laboratory for the generation of sulphuretted hydrogen. But the most important of the ferrous compounds is the sulphate, $FeSO_4, 7H_2O$, which is commonly known as green vitriol or copperas. It is prepared by dissolving iron in sulphuric acid, or by slowly oxidizing iron pyrites; and forms large, pale-green crystals which behave with regard to their water of crystallization precisely like the sulphates of zinc and magnesium. With tannin, or with solution of galls, ferrous sulphate strikes a deep-black color, on which account it is used in great quantities for the manufacture of ink. It also has some value as a disinfectant, acting as an absorbent of oxygen.

All ferrous salts tend to take up oxygen from the air, and to become converted into ferric compounds, which are mostly red or yellow. Ferric oxide, Fe_2O_3, is the important ore, hematite; and also, artificially prepared, is used both as a material for polishing glass and precious metals, and as a pigment under the name of Venetian-red. Jeweler's rouge and crocus-powder are merely ferric oxide. Several ferric hydroxides are found as mineral species, and are valuable ores. An artificial hydroxide, $Fe_2(OH)_6$, is produced by caustic alkalies in solutions of ferric salts, as a reddish-brown precipitate. It is used in some processes for purifying coal-gas, and as an antidote for arsenical poisoning. Iron-rust is another ferric hydroxide, produced by the joint action of air and water upon metallic iron. Ferric chloride, Fe_2Cl_6, and ferric sulphate, $Fe_2(SO_4)_3$, are both important ferric salts. The chloride is used as a reagent in the laboratory, and also in medicine as a material to stop bleeding. The sulphate unites with alkaline sulphates to form alums, which correspond perfectly to the similar salts of aluminum and chromium.

The magnetic oxide, Fe_3O_4, is a very important ore, and is also met with as *iron-scale* in the blacksmith-shops. By heating iron in dry steam it may be coated with a thin black film of this oxide and protected against rust. Fe_3O_4 is a neutral oxide, and may be regarded as $FeO + Fe_2O_3$. Iron pyrites, FeS_2, is a common mineral, which is sometimes called "fools' gold." It is yellow and metallic in appearance, but, unlike gold, it may be pulverized under a hammer. It is used as a source of copperas, and also in the manufacture of sulphuric acid.

EXPERIMENT 95.—Dissolve some iron filings in dilute sulphuric acid, and divide the solution into two parts. Add ammonia to one portion, and note the color of the *ferrous* hydroxide which is thrown down. Boil the other portion with a few drops of strong nitric acid, and observe the change of tint. Again precipitate with ammonia, and note the peculiarities of the *ferric* hydroxide which will be obtained. Nitric acid oxidizes ferrous compounds to the ferric state.

CHAPTER XXX.

NICKEL, COBALT, AND COPPER.

NICKEL and cobalt are comparatively rare metals, having a decided resemblance to iron. Both are white and malleable, but cobalt has a very slight reddish tinge. Both are strongly magnetic, and their specific gravity is not far from 9. The atomic weight of nickel is 58; that of cobalt is 59.

The chief supply of nickel comes from Germany, Pennsylvania, and New Caledonia, and quite recently valuable deposits of a nickel-ore have been found in Oregon. The ores are mostly sulphides, arsenides, and silicates of nickel, and the extraction of the metal is a somewhat complicated matter. It is used as an ingredient of small coins by several nations, and German silver is an alloy of copper, zinc, and nickel. Of late years the process of electroplating with nickel has assumed considerable importance. The metal forms a beautiful white surface which does not rust, and is chiefly applied to articles of copper, brass, or steel.

The compounds of cobalt and nickel resemble those of iron, except that their lower salts do not so readily oxidize to form the higher. The oxides CoO, NiO, Co_2O_3, Ni_2O_3, yield series of derivatives similar to the ferrous and ferric compounds. The nickelous salts are generally green, and the sulphate, $NiSO_4, 7H_2O$, the chloride, $NiCl_2, 6H_2O$, and the nitrate, $Ni(NO_3)_2, 6H_2O$ are the most important. The salt employed in nickel-plating is the double sulphate $NiSO_4, Am_2SO_4, 6H_2O$.

The cobaltous salts are remarkable in regard to their colors. They are rose-red when hydrated, blue when anhydrous. Heat cobalt sulphate, $CoSO_4, 7H_2O$, until its water of crystallization is expelled, and its red color will pass into the blue tint of $CoSO_4$.

EXPERIMENT 96.—Dissolve cobalt chloride in water, and with a small brush apply the solution to a sheet of white paper. When the latter is dry, scarcely any color can be perceived upon it, but by gently heating before a fire it will become distinctly blue. The solution, therefore, may be used as a "sympathetic ink"; and a letter written with it will be legible only when the paper is warm.

Some of the cobalt compounds are valuable colors, especially for glass and porcelain. Smalt blue is a silicate of cobalt, which withstands the highest temperatures of the porcelain oven. Thénard's blue contains the oxides of cobalt and aluminum. Rinmann's green consists of the oxides of cobalt and zinc.

EXPERIMENT 97.—Place a crystal of alum on a charcoal support, and heat it before the blow-pipe. Moisten the infusible residue with a drop of cobalt nitrate solution, and heat again. The mass will become blue. Repeat the experiment, using zinc oxide instead of alum, and a green will be produced. Magnesia, treated in the same way with cobalt nitrate, gives a pale rose. By cobalt compounds a borax bead is colored intensely blue.

COPPER, atomic weight 63.3, is a metal having some relationship to the iron group on one side, and closely allied to silver and mercury on the other. Like mercury, it forms two sets of compounds, a cuprous and a cupric series, but some of its salts are quite analogous to similar compounds of iron. The symbol, Cu, is from the Latin *cuprum*.

Copper is widely diffused in the mineral kingdom, both as native metal and in a great variety of compounds. Native copper is abundant in the Lake Superior mining region, and a single mass weighing four hundred and twenty tons was once found. Important ores of copper are cuprous sulphide, Cu_2S; the oxides, Cu_2O and CuO; bornite, Cu_3FeS_3; copper pyrites, $CuFeS_2$; and malachite, $CuCO_3$, $Cu(OH)_2$. The last-named mineral is often used as an ornamental green stone.

The process of extracting copper from its ores is generally somewhat complicated. The native metal, of course, only needs to be put through a refining operation in order to be prepared for market; and the oxides and carbonates of copper may be easily reduced by heating with carbon; but in most smelting-works the metallurgist has to deal with sulphides containing iron. These are commonly treated as follows: The ore is first roasted in a reverberatory furnace, whereby the cuprous sulphide is partly converted into oxide. It is then mixed with sand, or with a fusible silicate, and melted; the copper regains sulphur, while the iron is oxidized, and runs off as a part of the slag. The cuprous sulphide, or "coarse metal," thus obtained is re-roasted and re-melted, and so on, until all the iron contained in the ore has been slagged off, and only a pure cuprous sulphide, or "fine metal," remains. The latter is then partly oxidized by roasting, and the mixture of oxide and sulphide is finally fused; sulphur dioxide is driven off, and metallic copper is left behind.

$$2CuO + Cu_2S = 4Cu + SO_2.$$

In the Hunt and Douglas process the sulphides of copper are roasted, and then treated, in powder, with a solution of ferrous chloride. Copper goes into solution, and is afterward precipitated in the metallic state by the addition of scrap-iron. The latter reproduces ferrous chloride, which may be applied to another charge of ore, etc. This process is an interesting example of a class of metallurgical processes which are fast assuming industrial importance. The precipitation of copper by iron may be illustrated as follows:

EXPERIMENT 98.—Dip a piece of bright iron or steel into a solution of any salt of copper. Copper will immediately be deposited in a thin, red coating upon the surface of the other metal.

Copper is interesting on account of its being the only red metal. It is very malleable and ductile, and exceedingly tenacious; and, after silver, it is the best conductor for heat and electricity. Battery-wires and lightning-conductors are usually made of it. Its specific gravity is 8.945, and it melts at about 1,050° C. At very high temperatures it is slightly volatile; and its vapor, either free or in compounds, colors flame green. The best solvent for copper is nitric acid; boiling sulphuric acid dissolves it also; but hydrochloric acid attacks it only with difficulty.

Copper is not only useful by itself, but also in many alloys. Brass, bronze, German-silver, aluminum bronze, etc., have been already described.* Copper is very easily deposited by electrolysis, and this fact is applied in the process of electrotyping, as follows: A page of type, set up in the usual way, is first copied in wax or plaster. The mold thus obtained, which is a perfect impression of the type, is then dusted over with powdered graphite, in order to render it a conductor of electricity, and suspended in a solution of copper sulphate. It is connected by a copper wire with the zinc-pole of the battery, while the other pole terminates in a copper bar or plate, which is also immersed in the liquid. As the current passes, copper is deposited upon the mold in a coherent film of any desired thickness, and a perfect copy of the type is obtained. By this process copper may be deposited to any extent; and even colossal statues may be electrically copied by precipitating the metal gradually upon their plaster casts. In electro-metallurgy copper has many applications.†

The cuprous compounds have little importance, except that cuprous oxide, Cu_2O, is used for giving a ruby-red color to glass. Most of the cupric salts are green or blue when crystallized, but cupric sulphate, $CuSO_4, 5H_2O$, is white when anhydrous. This salt, which forms large blue crystals, may be transformed into a white powder by careful heating. It is the most important of the copper com-

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* See under zinc, tin, nickel, and aluminum.

† See Gore's work on electro-metallurgy, previously cited.

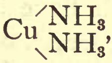
pounds, and is commonly known as blue vitriol. It is used in great quantities in galvanic batteries for telegraph lines, in electro-metallurgy, in calico-printing, in the manufacture of Paris green, etc.

Cupric oxide, CuO, is black; but the hydroxide, $Cu(OH)_2$, is light blue. The relations between them may be easily illustrated by experiment.

EXPERIMENT 99.—Dissolve cupric sulphate in water, and add a little caustic soda to the *cold* solution. A blue precipitate of $Cu(OH)_2$ will fall, which will be transformed into black CuO, upon boiling.

$$CuSO_4 + 2NaOH = Na_2SO_4 + Cu(OH)_2.$$
$$Cu(OH)_2 = CuO + H_2O.$$

Repeat the experiment, using ammonia-water instead of caustic soda. The precipitate at first formed will redissolve in an excess of the precipitant, yielding an intensely deep-blue solution. This reaction furnishes a most delicate test for copper.

In this experiment with ammonia a peculiar compound is formed having the formula $CuSO_4, 2NH_3$. With other copper salts other similar compounds will be produced; all of which may be regarded as salts of a peculiar complex base, called cuprammonium,  $Cu\begin{array}{l}\diagup NH_3\\ \diagdown NH_3\end{array}$, derived from two ammonium atoms by the replacement of two hydrogen atoms by one atom of dyad copper. Many such complex bases are known, and they have great theoretical interest.

All the copper compounds are very poisonous. Hence cooking utensils of copper, such as preserving-kettles and the like, should be used only with extreme care. They should always be kept clean and bright, and acid fruits or preserves should not be left long in contact with them. This statement applies also to brass. The dangerous pigments containing arsenic and copper were described in a previous chapter.

CHAPTER XXXI.

GOLD, AND THE PLATINUM GROUP.

GOLD, atomic weight 196.5, is almost invariably found in the uncombined state. The only exception is in the case of certain tellurides, which generally contain both gold and silver. To some extent, gold in dust, grains, or nuggets, is washed out from loose soil and gravel, or found imbedded in rock; but the larger yield is from invisible particles diffused through veins of iron pyrites or quartz. The gold-bearing rock is crushed to powder, and, if it contains much pyrites, is roasted; the mass is then agitated with mercury, which readily amalgamates with the more precious metal. The mercury is finally distilled off and recovered for use in future operations, while metallic gold remains behind.

Gold, thus obtained, is rarely pure. It generally contains some silver; and copper, iron, arsenic, and other metals are common impurities. When base metals are present, it is easily refined by forcing chlorine gas through it while in the melted state; the impurities form chlorides, which either volatilize or float in an easily removable scum, and absolutely pure gold remains below. From silver it is generally freed by a process known as *quartation.* The crude bullion is melted with an additional quantity of silver, so that it shall consist of three parts of the latter metal to one of gold; the alloy is then rolled into thin ribbons and treated with nitric acid; the silver is dissolved out as nitrate, and pure gold is obtained.

Gold is bright yellow in color, softer than silver, and malleable and ductile to an extraordinary degree. One grain of gold can be made to gild two miles of fine silver wire, or drawn into gold wire an eighth of a mile long. It may be beaten into leaves so thin that 280,000 would only make the thickness of one inch. These thin leaves transmit light, and, held between the eye and the sun, appear of a greenish color. To glass, finely divided gold imparts a fine ruby-red tint. The specific gravity of gold is 19.3, and it melts at about 1,100° C. For practical uses pure gold is too soft; hence it is always alloyed with copper or silver. The former alloy renders it ruddier, the latter makes it paler in color. The coin standard of the United States, for gold as well as for silver, is 900 fine—that is, 900 parts of gold to 100 of alloy. Jeweler's gold is generally less fine, and its character is indicated by a standard called the *carat*. Pure gold is said to be 24 carats fine; three fourths pure would therefore be 18 carats; two thirds fine would be 16 carats, etc. With mercury gold amalgamates very readily; hence gold rings should never be worn when quicksilver is being handled.

EXPERIMENT 100.—Put a drop of mercury upon a bit of gold-leaf. The latter will dissolve, forming a white amalgam.

Gold is insoluble in all acids, except the mixture known as *aqua regia*. It is trivalent, and forms two sets of compounds, of which the oxides Au_2O and Au_2O_3, and the chlorides AuCl and $AuCl_3$ are good examples. The symbol Au is from the Latin *aurum*. The aurous compounds are of slight importance only.

The trichloride, $AuCl_3$, is the most useful of the gold salts. It is formed whenever gold is dissolved in *aqua regia*, and may be obtained in orange-yellow deliquescent crystals which are sensitive to light. It is used in "toning" photographs, and in electroplating. As applied to gold the latter process is almost exactly like the one described under silver; only a solution of the double cyanide of gold and potassium is used, with a gold anode.

PLATINUM, atomic weight 195, is always more or less associated with five other metals, iridium, osmium, palladium, rhodium, and ruthenium. All these metals are quadrivalent, and together they are known as the platinum group. With one very rare exception * they are found in the free state, or rather alloyed with one another, and occasionally with gold.

Platinum was originally brought from the gold-washings of South America about the middle of the last century. Its name, from *platina*, is the Spanish diminutive of *plata*, silver, and hence it means "little silver." The greater part of the world's supply now comes from the Ural Mountains. The ore occurs in grains and small lumps, mixed with various impurities, from which it has to be separated by a complicated process of refining. It is a steel-white metal, fusible only at or above the temperature of the oxyhydrogen-flame, and of specific gravity 21.5.

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* The mineral laurite, ruthenium sulphide, found in Borneo.

Of all the other metals, iridium and osmium only are heavier, and that but a trifle; the specific gravity of osmium, which is heaviest of all, is 22.5.

Platinum is, like gold, insoluble in all acids except *aqua regia*. This property, together with its infusibility, renders it extremely useful for the construction of some pieces of chemical apparatus—such as dishes, crucibles, blow-pipe tips, foils, wire, etc. The stills used for concentrating sulphuric acid are made of platinum, and the metal is also employed as the negative element in Grove's galvanic battery. Without platinum utensils the chemical analysis of many minerals would be practically impossible. Commercial platinum is generally stiffened and hardened by the addition of a little iridium. Platinum-black is a very finely divided platinum, which possesses a remarkable power of condensing gases within its pores. One volume of this substance can absorb 800 volumes of oxygen; and hence it serves for some purposes as a powerful oxidizing agent.

The compounds of platinum are many, complicated, and theoretically interesting. There is a platinous series, corresponding to $PtCl_2$ and PtO; and a platinic series, represented by $PtCl_4$ and PtO_2. Platinic chloride, which is prepared by dissolving platinum in *aqua regia* and evaporating to dryness, is the most important of these compounds. It is used in chemical analysis for the detection of potassium and ammonium, and their separation from other bases. Potassium chloroplatinate, K_2PtCl_6 or $2KCl + PtCl_4$, is a yellow precipitate often produced in the laboratory.

The other metals of the group are rare and of little relative importance. An alloy of iridium and osmium, called iridosmine, is often found in gold-washings, and forms brilliant grains which are harder than steel, and are used for tipping gold pens. A process has recently been devised for fusing them with phosphorus, and so obtaining a very hard and refractory metal which may be used for a variety of practical purposes. Iridium-plating has very lately been patented, and may soon become a useful industry.

Platinum, iridium, and osmium are near each other in atomic weight and specific gravity. Palladium, rhodium, and ruthenium form another trio, having atomic weights from 103 to 106, and specific gravities from 11 to 12. Palladium is a silver-white, easily workable metal, which has been used to a limited extent in philosophical apparatus. It has the property of absorbing hydrogen, and forming what is apparently an *alloy* with the latter. This *occluded* hydrogen is commonly regarded as metallic, and is sometimes called *hydrogenium*.

PART II.

ORGANIC CHEMISTRY.

CHAPTER XXXII.

PRELIMINARY OUTLINE.

In the early days of chemistry a sharp distinction was drawn between the compounds derived from plants and animals and those obtained from the inorganic or mineral kingdom. Such substances as sugar, starch, the fruit acids, and albumen, together with many other bodies directly derived from them, were termed organic; while the minerals, metals, elements, and the commoner salts, all of non-living origin, were classed as inorganic. These classes of substances were regarded as perfectly distinct; for it was thought that in the production of organic bodies some peculiar vital force was involved, and that no artificial means could ever be discovered for their preparation. In 1828, however, Woehler effected the synthesis of a well-known organic compound, urea, from wholly inorganic materials; and since then a vast number of similar syntheses have been successfully accomplished. One of the latest triumphs of synthetic chemistry has been the artificial preparation of indigo. The old boundary between the organic and the inorganic has been thoroughly broken down, and to-day the division is merely one of convenience.

Organic compounds, so called, are remarkable for their great number and complexity. They all agree in containing carbon, generally in union with hydrogen, oxygen, nitrogen, or all three. Occasionally they contain sulphur and phosphorus also; and many of the artificial products contain chlorine, bromine, iodine, boron, silicon, arsenic, or metals. All of them, however, owe their chief characteristics to carbon; and on this account organic chemistry is now commonly defined as the chemistry of the carbon compounds. Carbon, by virtue of its quadrivalence, is capable of building up complicated molecular structures; and in doing so it seems to combine with itself to form chains or rings of carbon-atoms, that serve as centers around which, in accordance with the laws of valency, other elements can be grouped. This property of carbon will become evident as we study its compounds.

In general, organic substances may be most conveniently regarded as derived from compound radicles, which, in most cases, are hydrocarbons having unsatisfied bonds of valency. Cyanogen, however, and carbon monoxide, being unsaturated compounds, play an important part in organic chemistry; and so also, but in a different way, do ammonia and ammonium. From the last two substances, and from the compound NO_2, many of the more important nitrogenous bodies are derived.

Although hundreds of hydrocarbons are known, and an almost infinite number are theoretically possible, they may all be easily arranged in a small number of comparatively simple series. Methane, for example, CH_4, is the compound of carbon and hydrogen containing the highest proportion of the latter element; and in it the four bonds of the one are exactly satisfied by the corresponding number of the other. This compound is, however, the first member of a series; the higher terms being C_2H_6, C_3H_8, C_4H_{10}, C_5H_{12}, and so on up to $C_{35}H_{72}$. Here each hydrocarbon differs from the one which precedes it by one atom of carbon and two of hydrogen; the second being the first plus CH_2, and so on as far as the series extends. Such a series is known as an *homologous series;* and it may be represented by one general formula C_nH_{2n+2}. All other hydrocarbons fall into similar series, and for each series a similar formula may be assigned, as is shown in the following scheme:

Series 1.	C_nH_{2n+2}.	Lowest member known,	CH_4.
" 2.	C_nH_{2n}.	" " "	C_2H_4.
" 3.	C_nH_{2n-2}.	" " "	C_2H_2.
" 4.	C_nH_{2n-4}.	" " "	C_5H_6.
" 5.	C_nH_{2n-6}.	" " "	C_6H_6.
" 6.	C_nH_{2n-8}.	" " "	C_8H_8.
" 7.	C_nH_{2n-10}.	" " "	C_8H_6.
" 8.	C_nH_{2n-12}.	" " "	$C_{10}H_8$.
" 9.	C_nH_{2n-14}.	" " "	$C_{12}H_{10}$.
" 10.	C_nH_{2n-16}.	" " "	$C_{14}H_{12}$.
" 11.	C_nH_{2n-18}.	" " "	$C_{14}H_{10}$.
" 12.	C_nH_{2n-20}.	" " "	$C_{17}H_{14}$.
" 13.	C_nH_{2n-22}.	" " "	$C_{16}H_{10}$.
" 14.	C_nH_{2n-24}.	" " "	$C_{18}H_{12}$.
" 15.	C_nH_{2n-26}.	" " "	$C_{20}H_{14}$.
" 16.	C_nH_{2n-28}.	" " "	———
" 17.	C_nH_{2n-30}.	" " "	$C_{22}H_{14}$.
" 18.	C_nH_{2n-32}.	" " "	$C_{26}H_{20}$.

All possible hydrocarbons are covered by this system of formulæ, although structural formulæ of a more definite kind are needed to bring out the relations of these compounds fully. For one series no representative has as yet been discovered, and in several series the lowest possible members are not known; but some of these gaps will, doubtless, be filled in due time.

From many of these hydrocarbons other compounds are derived by a process known as *substitution*, in which atoms of hydrogen are successively replaced by atoms of other univalent elements like chlorine, bromine, or iodine. Thus, from methane, CH_4, we get substitution series as follows:

1. CH_4. CH_3Cl. CH_2Cl_2. $CHCl_3$. CCl_4.
2. CH_4. CH_3Br. CH_2Br_2. $CHBr_3$. CBr_4.
3. CH_4. CH_3I. CH_2I_2. CHI_3. CI_4.

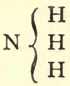
For benzene, C_6H_6, the chlorine substitution series is even more striking; thus:

C_6H_5. C_6H_5Cl. $C_6H_4Cl_2$. $C_6H_3Cl_3$. $C_6H_2Cl_4$. C_6HCl_5. C_6Cl_6.

In many cases compound radicles serve as agents of substitution, as in the case of the univalent group NO_2, which enters into numerous important substances. A few examples will suffice:

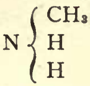
C_6H_6.	$C_6H_5(NO_2)$.	$C_6H_4(NO_2)_2$.
Benzene.	Nitrobenzene.	Dinitrobenzene.
$C_3H_8O_3$.	$C_3H_5(NO_2)_3O_3$.	Etc.
Glycerin.	Trinitroglycerin.	

Still another class of substitution compounds of the highest importance is derived from ammonia, NH_3, by replacing hydrogen with such radicles as methyl, CH_3, or ethyl, C_2H_5. They are called *amines*, and are constituted as follows:



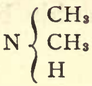
$$N\begin{cases}H\\H\\H\end{cases}$$

Ammonia.



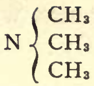
$$N\begin{cases}CH_3\\H\\H\end{cases}$$

Methylamine.



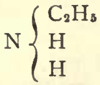
$$N\begin{cases}CH_3\\CH_3\\H\end{cases}$$

Dimethylamine.



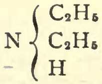
$$N\begin{cases}CH_3\\CH_3\\CH_3\end{cases}$$

Trimethylamine.



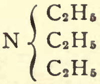
$$N\begin{cases}C_2H_5\\H\\H\end{cases}$$

Ethylamine.



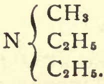
$$N\begin{cases}C_2H_5\\C_2H_5\\H\end{cases}$$

Diethylamine.



$$N\begin{cases}C_2H_5\\C_2H_5\\C_2H_5\end{cases}$$

Triethylamine.



$$N\begin{cases}CH_3\\C_2H_5\\C_2H_5.\end{cases}$$

Etc.

Diethylmethylamine.

Similarly, from PH_3 we get a series of phosphines; from AsH_3, arsines; from SbH_3, stibines, and so on. Compounds of this kind are exceedingly numerous, and others like them are derived from ammonium, NH_4:

NH_4Cl.	$N(CH_3)_4Cl$.	$N(C_2H_5)_4Cl$.
Ammonium chloride.	Tetramethylammonium chloride.	Tetrethylammonium chloride.

These few examples will suffice for present purposes.

One other noteworthy feature of organic compounds demands a brief consideration at this point —namely, *isomerism.* It often happens that two or more entirely different substances are represented by the same formula, both containing precisely the same elements, united in precisely the same proportions. Such compounds are called *isomeric,* and owe their differences to different groupings of the atoms within the molecules. Just as the same letters may be so arranged as to spell several different words, so the same atoms may be grouped in several dissimilar clusters. For example, the *empirical* formula C_2H_6O represents two substances —the one a gas, the other a liquid. One is the oxide of the univalent radicle methyl, the other is ethyl hydroxide, or common alcohol; and their formulæ, written side by side, show the difference clearly:

$(CH_3)_2O$.	C_2H_5OH.
Methyl oxide.	Alcohol.

In this instance both compounds have the same molecular weight, and the same vapor density. In some cases of imperfect isomerism, these properties may differ in such a way that the compounds may form a series of which the higher members shall have molecular weights, even multiples of the lowest. Such a case is furnished by the *polymeric* series of hydrocarbons C_nH_{2n}, in which, although all of its members have the same percentage composition, the molecular weights vary widely. Another example of *polymerism* is afforded by the compounds C_2H_2, C_6H_6, and C_8H_8, which represent three different series. Other instances of isomerism and polymerism will be considered by-and-by.

CHAPTER XXXIII.

CYANOGEN AND CARBONYL COMPOUNDS.

FREE cyanogen, C_2N_2 or $(CN)_2$, is prepared by heating mercuric cyanide. It is a colorless gas with an odor resembling peach-kernels, and it burns with a beautiful purple flame. In the chapter upon carbon it was shown that this gas behaved much like an element of the chlorine group, and that the molecules $(CN)_2$ and Cl_2 had many points of similarity. Thus we have a hydrocyanic acid, HCN, and a series of metallic cyanides such as KCN, $Hg(CN)_2$, and so on. Some of these compounds have practical importance.

Hydrocyanic acid, HCN, commonly known as prussic acid, is obtained whenever a cyanide is treated with a strong acid like sulphuric. In this respect it resembles hydrochloric acid, as the subjoined equations show:

$$H_2SO_4 + 2NaCl = 2HCl + Na_2SO_4.$$
$$H_2SO_4 + 2NaCN = 2HCN + Na_2SO_4.$$

Practically, the yellow salt known as potassium ferrocyanide is distilled with dilute sulphuric acid in a glass retort, and an aqueous solution of hydrocyanic acid is collected in the receiver. This acid has a strong odor resembling peach-kernels or bitter-almonds, and is intensely poisonous. A single drop of the pure compound, which is a volatile liquid boiling at 26.5°, placed upon the tongue of a small animal, such as a cat or rabbit, will cause death almost instantaneously. It is the most sudden and one of the most fatal of all known poisons, and its dangerous qualities are shared in a less degree by many of its derivatives. It is very unstable, and can be preserved only in dilute solutions. As an acid it is exceedingly weak, and may be expelled with ease from most of its compounds.

Potassium cyanide, KCN, is a white salt of considerable importance. Great quantities of it are used in the processes of gold and silver plating. It is dangerously poisonous, and should be handled with extreme care. It has, faintly, the characteristic peach-kernel odor. Silver cyanide, $AgCN$, is a white precipitate closely resembling the chloride.

With some of the metals of high valency cyanogen forms very curious and important double salts. Of these, potassium *ferrocyanide*, $K_4Fe(CN)_6$, is the most useful and noteworthy. To prepare this salt, iron-filings, potash, and nitrogenous matter, such as scraps of horn, hides, leather-clippings, hair, or refuse feathers, are heated together to the temperature of fusion. The cooled mass is afterward treated with water, and the solution evaporated to the point of crystallization. The ferrocyanide is thus obtained in large yellow crystals containing three molecules of water. It is sometimes called the "yellow prussiate of potash," and is not poisonous. Its uses may be illustrated by experiment:

EXPERIMENT 101.—To a solution of potassium ferrocyanide add a solution of ferrous sulphate. A pale-bluish precipitate will form, which will rapidly change to deep blue. Repeat the experiment, using a ferric salt, and a deep-blue precipitate will be produced at once.

There are several different compounds producible in the foregoing manner. One of them, $Fe_5(CN)_{12}$, is an important paint, Prussian blue; and another, derived from the latter, $Fe_7(CN)_{18}$, is called Williamson's blue. The chief use of potassium ferrocyanide is in the manufacture of these colors. With solutions of copper, potassium ferrocyanide gives a very characteristic reddish-brown precipitate; and by the production of this, very small traces of copper may be detected.

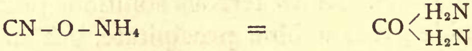
Potassium ferrocyanide may be regarded as the potassium salt of hydroferrocyanic acid, $H_4Fe(CN)_6$. This acid is well known, and forms a large series of salts. Having four replaceable hydrogen-atoms, it is tetrabasic. In none of the ferrocyanides do the ordinary tests for iron reveal the presence of the later metal. It is completely masked.

By passing chlorine into a solution of the ferrocyanide a salt called potassium ferricyanide is produced. This compound forms large red crystals having the formula $K_3Fe(CN)_6$, and from it a hydroferricyanic acid and a series of corresponding salts may be derived. With ferrous solutions potassium ferricyanide gives a blue precipitate, but in ferric compounds it only produces a slight brownish coloration. It is a useful reagent in distinguishing between ferrous and ferric compounds, and it is also employed in the preparation of blue paints. Like iron, cobalt also forms interesting series of cobalto and cobalticyanides, and most of the metals of the iron and platinum groups behave in a similar way. The platinocyanides are among the most beautiful compounds known to chemistry.

With oxygen and sulphur, cyanogen forms two quite similar acids—namely, cyanic acid, CNOH, and sulphocyanic acid, CNSH. Potassium sulphocyanate, CNSK, is a white salt which yields a magnificent red coloration with ferric solutions. It gives no reaction with ferrous salts, and serves as a very delicate reagent for the detection of ferric iron.

Some of the cyanogen compounds display in a remarkable degree the power of polymerization. For example, hydrocyanic acid, CNH, readily changes into a solid compound, $C_3N_3H_3$, called trihydrocyanic acid. Cyanic acid, CNOH, similarly is related to cyanuric acid, $C_3N_3O_3H_3$, and to a third polymer of unknown molecular weight called cyamelide. So, also, there are two chlorides of cyanogen, one a liquid, CNCl; the other a solid, $C_3N_3Cl_3$. On account of this tendency to polymerize, the derivatives of cyanogen are very numerous and complicated.

When ammonium cyanate, NH_4CNO, is heated, its atoms undergo a peculiar rearrangement, and it is transformed into the isomeric compound, carbamide or urea:



$$CN-O-NH_4 \quad = \quad CO\begin{matrix} \diagup H_2N \\ \diagdown H_2N \end{matrix}$$

Ammonium cyanate. Carbamide.

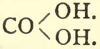
The latter compound, as will be seen, may be regarded as derived from two atoms of ammonia, by replacing one hydrogen-atom from each by the bivalent radicle CO. This radicle, known in inorganic chemistry as carbon monoxide, is called *carbonyl* for brevity, and occurs in many organic compounds. Some of its simpler derivatives are as follows:

$CO.O.$

Carbonyl oxide, or carbon dioxide.

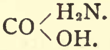
$COCl_2.$

Carbonyl chloride.



$CO\begin{array}{l}\diagup OH.\\ \diagdown OH.\end{array}$

Carbonic acid.

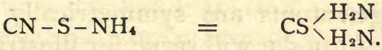


$CO\begin{array}{l}\diagup H_2N.\\ \diagdown OH.\end{array}$

Carbamic acid.

Carbamide is a white solid which is found in many animal juices, and has great theoretical interest. It was the first organic compound ever produced by synthesis from inorganic matter. It acts like a weak base, uniting with nitric and oxalic acids to form a nitrate and an oxalate, and it also yields many complex derivatives.

If we heat ammonium sulphocyanate, NH_4CNS, instead of the cyanate, a sulphocarbamide or sulphourea will be formed.



$$CN-S-NH_4 \quad = \quad CS\begin{array}{l}\diagup H_2N\\ \diagdown H_2N.\end{array}$$

Ammonium sulphocyanate. Sulphourea.

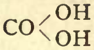
This compound contains the radicle *sulphocarbonyl*, CS, which yields derivatives similar in structure to those obtained from CO. For example:

$COCl_2.$

Carbonyl chloride.

$CSCl_2.$

Sulphocarbonyl chloride.



$CO\begin{array}{l}\diagup OH\\ \diagdown OH\end{array}$

Carbonic acid.

$CS\begin{array}{l}\diagup SH\\ \diagdown SH.\end{array}$

Sulphocarbonic acid.

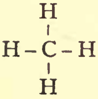
The greater number of these compounds are interesting only from a theoretical point of view. In the present instance they serve to illustrate in a simple way the convenience of structural formulæ. By means of the latter, many relations between different substances may be most clearly brought out, and the memory can thus be aided to a wonderful degree.

CHAPTER XXXIV.

THE METHANE SERIES.

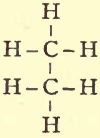
THE methane or marsh-gas series of hydrocarbons, $CnH2n + 2$, is of the utmost importance, both in theory and in practical work. Some of its members constitute the greater part of petroleum; and from other members such noteworthy substances as alcohol, ether, chloroform, and acetic acid, are derived. Structurally, the series is very simple, the carbon-atoms forming a regular chain around which the hydrogen-atoms are symmetrically arranged. A very few formulæ will serve for illustration:

Methane, CH_4.



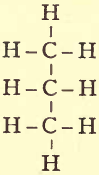
$$\begin{array}{c} H \\ | \\ H-C-H \\ | \\ H \end{array}$$

Ethane, C_2H_6.



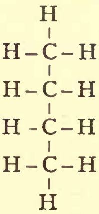
$$\begin{array}{c} H \\ | \\ H-C-H \\ | \\ H-C-H \\ | \\ H \end{array}$$

Propane, C_3H_8.



$$\begin{array}{c} H \\ | \\ H-C-H \\ | \\ H-C-H \\ | \\ H-C-H \\ | \\ H \end{array}$$

Butane, C_4H_{10}.



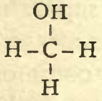
$$\begin{array}{c} H \\ | \\ H-C-H \\ | \\ H-C-H \\ | \\ H-C-H \\ | \\ H-C-H \\ | \\ H \end{array}$$

And so on, regularly, up to $C_{35}H_{72}$. After butane the hydrocarbons of this series receive numerical names, based upon the number of carbon-atoms which they contain. Thus, C_5H_{12} is pentane, C_6H_{14} is hexane, C_7H_{16} is heptane, $C_{10}H_{22}$ is decane, etc.

In properties, these hydrocarbons vary regularly.

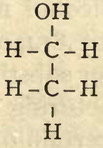
Methane, which was described under carbon, is a gas, and ethane, propane, and butane are also gaseous. Pentane is a liquid boiling at 38°, hexane boils at 70°, and so on through a series of liquids growing less and less volatile as we ascend, until at last we come to solid, waxy compounds which are known as paraffins. The whole series is sometimes called the paraffin group. Paraffin itself, such as is used for making candles, is a mixture of these higher hydrocarbons; coal-oil, or petroleum, consists chiefly of the liquid members of the series. The latter are separated by a process of distillation, and the mixture which distills over at comparatively low temperatures is known as naphtha or gasoline. Above 170°, the distillate is used for illuminating oil or kerosene; higher still, heavier and denser products are obtained, which serve for lubricating machinery. Kerosene which has not been carefully freed from the more volatile hydrocarbons is dangerous, and none should be used which gives off inflammable vapor at temperatures below 110° Fahr. Such vapors, like fire-damp, form explosive mixtures with air.

If, by proper reactions, we replace one atom of hydrogen in each of the foregoing hydrocarbons by a hydroxyl group, –O–H, we shall obtain a series of most important compounds which are called alcohols. Thus:



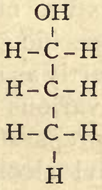
$$\begin{array}{c}\text{OH}\\ |\\ \text{H}-\text{C}-\text{H}\\ |\\ \text{H}\end{array}$$

CH_4O, methyl alcohol.



$$\begin{array}{c}\text{OH}\\ |\\ \text{H}-\text{C}-\text{H}\\ |\\ \text{H}-\text{C}-\text{H}\\ |\\ \text{H}\end{array}$$

C_2H_6O, ethyl alcohol.



$$\begin{array}{c}\text{OH}\\ |\\ \text{H}-\text{C}-\text{H}\\ |\\ \text{H}-\text{C}-\text{H}\\ |\\ \text{H}-\text{C}-\text{H}\\ |\\ \text{H}\end{array}$$

C_3H_8O, propyl alcohol.

And so on through the series. These alcohols may be conveniently regarded as the hydroxides of certain radicles, of which methyl, CH_3, ethyl, C_2H_5, and amyl, C_5H_{11}, are the most commonly encountered. These radicles do not exist in the free state, but their derivatives are of the highest importance; and most of them may be easily compared with the compounds of the univalent metals. Thus:

KOH.	CH_3OH.	C_2H_6OH.	$C_5H_{11}OH$.	Etc.
K_2O.	$(CH_3)_2O$.	$(C_2H_5)_2O$.	$(C_5H_{11})_2O$.	"
KCl.	CH_3Cl.	C_2H_5Cl.	$C_5H_{11}Cl$.	"
KNO_3.	CH_3NO_3.	$C_2H_5NO_3$.	$C_5H_{11}NO_3$.	"

These *alcoholic salts* are mostly liquids, and are called ethers. Their names, except in the series of alcohols, are precisely like those used in inorganic chemistry—as, for example, methyl chloride, ethyl oxide, propyl nitrate, amyl sulphate, etc. Nearly every acid, organic or inorganic, can unite with these radicles to form such ethers.

Three of the alcohols—namely, those of methyl, ethyl, and amyl—have practical importance, and therefore deserve especial mention. Methyl alcohol, CH_3OH, commonly called wood-spirit, is a colorless liquid obtained by the dry distillation of wood. The latter, when distilled at a high temperature, yields a variety of liquid products, and from the mixture methyl alcohol may be separated. It has a specific gravity of .814, and boils at 55°, and is used partly as a cheaper substitute for common alcohol in various manufacturing processes, and partly in the preparation of certain of the aniline colors.

Ethyl alcohol, C_2H_5OH, is the compound of this series to which in common life the name of alcohol is especially applied. Although it may be obtained from ethane, it is practically prepared only by the fermentation of saccharine and starchy bodies, such as cane-sugar, glucose, and the starch of potatoes or grain. These compounds, dissolved in water, are fermented by yeast, and a weak solution of alcohol is thus obtained. The latter is then concentrated by distillation, the process being repeated until an alcohol containing only about 10 per cent of water passes over. To obtain pure or "absolute" alcohol the commercial product is again distilled over caustic lime, which serves to retain the water.

EXPERIMENT 102.—Mix alcohol and water in equal proportions, place the mixture in a glass retort, and distill until one half has passed over into the receiver. Inasmuch as alcohol boils at 78.4° and water at 100°, the distillate will be found to contain most of the alcohol, while the portion remaining in the retort will be mainly water. Now repeat the operation with the distillate, again distilling one half, and a still stronger alcohol will be obtained. This process, which is known as *fractional distillation*, is continually employed in the laboratory for separating liquids of different volatility. The most volatile distill first, the least volatile remaining longest behind.

Pure alcohol is a colorless, inflammable liquid of specific gravity .806. It boils at 78.4°, but has never been frozen;* hence its use in thermometers intended for registering temperatures below the freezing-point of mercury. It has a peculiar spirituous smell and a burning taste, and in the pure state is poisonous. In a diluted condition it is used as a

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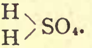
* Since this paragraph was written, alcohol has been frozen. At — 130.5° C., it solidifies to a white mass.

stimulant, and it is the intoxicating principle of all wines, spirits, and malt-liquors. Beer and ale contain from 4 to 7 per cent of alcohol; wine from 6 to 20 per cent; rum, brandy, and whisky from 40 to 50 per cent. The stronger commercial alcohol, or spirits of wine, contains from 50 per cent upward, and is used as an antiseptic, as a burning-fluid, as a solvent for gums and resins, in the manufacture of varnishes, perfumery, and medicinal preparations, and for a great variety of other practical purposes. To the chemist it is one of the most useful of chemical substances.

Amyl alcohol, $C_5H_{11}OH$, occurs as an impurity in spirits distilled from potatoes. It is commonly known as the chief constituent of a disagreeable mixture called fusel-oil. When pure, amyl alcohol is a colorless liquid which boils at 131°, and has a peculiarly suffocating odor. It is used in the preparation of valeric acid and some of its ethers.*

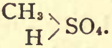
Propyl alcohol, C_3H_7OH, and butyl alcohol, C_4H_9OH, lie between ethyl and amyl alcohols. Cetyl alcohol, $C_{16}H_{33}OH$, is a *solid* compound derived from spermaceti; and melissyl alcohol, $C_{30}H_{61}OH$, is one of the constituents of beeswax. Like the higher hydrocarbons of the methane series, the higher alcohols and their derivatives are solid.

When common alcohol is cautiously mixed with strong sulphuric acid, a compound known as ethylsulphuric acid is formed. This is the type of a series of acids, constituted as follows:



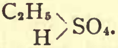
$\left.\begin{matrix}H\\H\end{matrix}\right\rangle SO_4.$

Sulphuric.



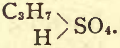
$\left.\begin{matrix}CH_3\\H\end{matrix}\right\rangle SO_4.$

Methylsulphuric.



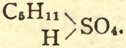
$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\rangle SO_4.$

Ethylsulphuric.



$\left.\begin{matrix}C_3H_7\\H\end{matrix}\right\rangle SO_4.$

Propylsulphuric.



$\left.\begin{matrix}C_5H_{11}\\H\end{matrix}\right\rangle SO_4.$

Amylsulphuric.

etc.

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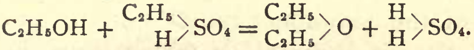
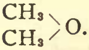
* See next chapter.

Heated with an additional quantity of alcohol, ethylsulphuric acid undergoes a further change, and ethyl oxide is formed. At the same time sulphuric acid is reproduced, ready to act upon a fresh portion of alcohol; thus:



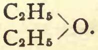
$$C_2H_5OH + \begin{matrix}C_2H_5\\H\end{matrix}\Big\rangle SO_4 = \begin{matrix}C_2H_5\\C_2H_5\end{matrix}\Big\rangle O + \begin{matrix}H\\H\end{matrix}\Big\rangle SO_4.$$

These reactions are applied on a large scale to the manufacture of ethyl oxide, which is commonly known as *ether.** This is a colorless liquid of peculiar odor, specific gravity .74, and boiling-point 34.5°. Its chief and important use as an anæsthetic, for preventing the pain of surgical operations, is well known. Allied to it are other ethereal oxides, which the subjoined formulæ may serve to illustrate:



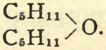
$$\begin{matrix}CH_3\\CH_3\end{matrix}\Big\rangle O.$$

Methyl ether.



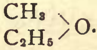
$$\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\Big\rangle O.$$

Ethyl ether.



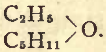
$$\begin{matrix}C_5H_{11}\\C_5H_{11}\end{matrix}\Big\rangle O.$$

Amyl ether.



$$\begin{matrix}CH_3\\C_2H_5\end{matrix}\Big\rangle O.$$

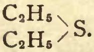
Methylethyl ether.



$$\begin{matrix}C_2H_5\\C_5H_{11}\end{matrix}\Big\rangle O.$$

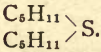
Ethylamyl ether.

The fourth and fifth of these formulæ represent *mixed* ethers. Many such compounds are possible. Besides these there are similar bodies containing sulphur, most of which are liquids of exceedingly nauseous odor. Their derivation may be illustrated thus:



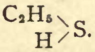
$$\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\Big\rangle S.$$

Ethyl sulphide.



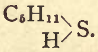
$$\begin{matrix}C_5H_{11}\\C_5H_{11}\end{matrix}\Big\rangle S.$$

Amyl sulphide.



$$\begin{matrix}C_2H_5\\H\end{matrix}\Big\rangle S.$$

Ethyl hydrosulphide.



$$\begin{matrix}C_5H_{11}\\H\end{matrix}\Big\rangle S.$$

Amyl hydrosulphide.

The hydrosulphides resemble the alcohols in structure, and are called mercaptans.

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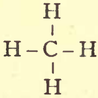
* Erroneously called "sulphuric ether" in commerce. The true sulphuric ether is ethyl sulphate, $(C_2H_5)_2SO_4$.

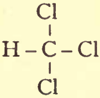
By the action of hydrochloric acid on the alcohols, the chlorides of the corresponding radicles may be produced. With bromine and iodine, in presence of a little phosphorus, the alcohols yield similar bromides and iodides. Methyl chloride, CH_3Cl, is a gas; but the other chlorides, bromides, and iodides of the commoner radicles of this series are volatile liquids resembling chloroform in odor. These compounds are often of use as steps in the preparation of others.

When methyl or ethyl alcohol is heated with bleaching-powder, chloroform is produced. This compound, $CHCl_3$, is a clear liquid of specific gravity 1.52, and an agreeable smell. It boils at 62°. Like ether, it is an important anæsthetic, but is less safe. Iodoform, CHI_3, is a yellow solid of some value in medicine. Both of these compounds are simple derivatives of methane:



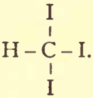
$$\begin{array}{c} H \\ | \\ H-C-H \\ | \\ H \end{array}$$

Methane.



$$\begin{array}{c} Cl \\ | \\ H-C-Cl \\ | \\ Cl \end{array}$$

Chloroform.



$$\begin{array}{c} I \\ | \\ H-C-I. \\ | \\ I \end{array}$$

Iodoform.

CHAPTER XXXV.

THE FATTY ACIDS.

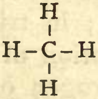
By the action of oxidizing agents upon the foregoing alcohols, two new series of compounds may be obtained. The reactions, with any given alcohol, are as follows: First, two atoms of hydrogen are withdrawn, forming water, and leaving a compound called an aldehyde:

$$C_2H_6O + O = C_2H_4O + H_2O.$$

By further oxidation the aldehyde takes up an atom of oxygen, and an acid is produced:

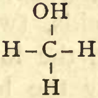
$$C_2H_4O + O = C_2H_4O_2.$$

The relations of these sets of compounds to each other, and to the methane series, may be represented structurally:



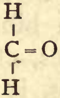
$$\begin{array}{c} H \\ | \\ H-C-H \\ | \\ H \end{array}$$

Methane.



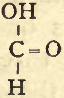
$$\begin{array}{c} OH \\ | \\ H-C-H \\ | \\ H \end{array}$$

Methyl alcohol.



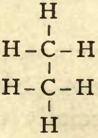
$$\begin{array}{l} H \\ | \\ C=O \\ | \\ H \end{array}$$

Formaldehyde.



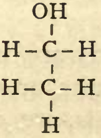
$$\begin{array}{l} OH \\ | \\ C=O \\ | \\ H \end{array}$$

Formic acid.



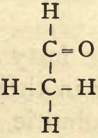
$$\begin{array}{c} H \\ | \\ H-C-H \\ | \\ H-C-H \\ | \\ H \end{array}$$

Ethane.



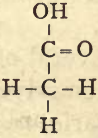
$$\begin{array}{c} OH \\ | \\ H-C-H \\ | \\ H-C-H \\ | \\ H \end{array}$$

Ethyl alcohol.



$$\begin{array}{c} H \\ | \\ C=O \\ | \\ H-C-H \\ | \\ H \end{array}$$

Acetaldehyde.



$$\begin{array}{c} OH \\ | \\ C=O \\ | \\ H-C-H \\ | \\ H \end{array}$$

Acetic acid.

Thus, corresponding to every hydrocarbon in the methane series, we have an alcohol, an aldehyde (*al*cohol *dehyd*rogenatum), and an acid. The aldehydes are quite unstable bodies, and the one derived from common alcohol is the best known. It is a very volatile liquid, having a peculiar odor, which may be recognized whenever alcohol is dropped upon chromic acid. Its uses are few.

The acids of this series, however, are important. The lower members are volatile liquids, the higher, above $C_{10}H_{20}O_2$, are waxy or greasy solids. Inasmuch as some of them are essential constituents of fats and oils, the entire series has been named the fatty acids. The more important among them are the following:

Formic	acid,	CH_2O_2,	or $HCOOH$.	Boils at	100°.
Acetic	“	$C_2H_4O_2$,	“ CH_3COOH.	“ “	118°.
Propionic	“	$C_3H_6O_2$,	“ C_2H_5COOH.	“ “	140°.
Butyric	“	$C_4H_8O_2$,	“ C_3H_7COOH.	“ “	163°.
Valeric	“	$C_5H_{10}O_2$,	“ C_4H_9COOH.	“ “	185°.
Stearic	“	$C_{18}H_{36}O_2$,	“ $C_{17}H_{35}COOH$.	Melts at	69°.

In each of these acids we find the group COOH, or, in detail, $O{=}C{-}OH$, which is characteristic of organic acids. In monobasic acids like these, it occurs once; in bibasic acids, twice; in tribasic acids, three times, etc. In the formation of salts from these acids, it is only the hydrogen of the COOH group which is replaceable by metals or by bases.

Several of the fatty acids are important, either by themselves or in their salts or ethers. Stearic, margaric, and palmitic acids, are especially useful in fats, oils, and soaps, and will be considered in another chapter. Acetic acid, or vinegar, merits a detailed notice here. It is commonly prepared by the oxidation of dilute alcohol, such as cider, wine, or weak whisky. In cider and wine the alcoholic stage of fermentation is followed by an *acetous* stage, and the change from alcohol to acetic acid takes place without artificial assistance. This transformation of cider into vinegar is a matter of every-day observation; but only a small part of the vinegar in use is made in this way. On a large scale, very weak alcohol, such as the fermented mash from which spirit is to be distilled, is allowed to trickle slowly through large casks filled with wood-shavings. The alcohol, diffused over the shavings, exposes a very large surface to the oxidizing action of the air, which latter enters the cask freely through holes in the sides, and escapes through other holes in the top. The oxidation from alcohol to acetic acid is thus effected much more rapidly than by the tedious process of fermentation which was previously referred to.

FIG. 52.—Manufacture of Vinegar.

EXPERIMENT 103.—Distill a little vinegar from a glass retort. The distillate will be a weak acetic acid free from the impurities which gave the vinegar its color. Pure acetic acid may be prepared by distilling an acetate with sulphuric acid. A sulphate will be formed and acetic acid set free.

Perfectly pure acetic acid is a colorless liquid which solidifies to an ice-like mass at 17°. It has the odor of vinegar to an increased degree, and has all the properties of a strong acid. Dissolve sodium or calcium carbonate in vinegar, and you will obtain, with vigorous effervescence, a solution of sodium or calcium acetate. Sodium acetate is a useful laboratory reagent; lead acetate is the well-known "sugar of lead"; copper acetate is "verdigris." These salts (omitting water of crystallization) are formed from acetic acid by substitution of hydrogen, precisely as in the domain of inorganic chemistry. Thus:

Acetic acid,		$C_2H_4O_2$.
Sodium	acetate,	$C_2H_3O_2Na$.
Potassium	"	$C_2H_3O_2K$.
Lead	"	$(C_2H_3O_2)_2Pb$.
Copper	"	$(C_2H_3O_2)_2Cu$.

With the alcohols of the methane series the fatty acids yield a large number of compound ethers. These are interesting, both because of their properties and on account of their bearing upon the subject of isomerism. Practically, several of them are made for use in the manufacture of flavoring extracts. For instance, ethyl butyrate has the taste and odor of pineapples; amyl acetate affords a close imitation of bananas; amyl valerate is made as "apple-oil," etc. The peculiar flavors of many fruits are doubtless due to the existence, naturally formed, of some of these same ethers. Each ether is isomeric with one of the acids, and in some cases several ethers are isomeric with each other. The cause of the isomerism, however, is easily understood, as the following formulæ for the compounds $C_7H_{14}O_2$ will show :

Œnanthylic acid,	C_6H_{13}, COOH	=	$C_7H_{14}O_2$.
Hexyl formate,	C_6H_{13}, CHO_2	=	“
Amyl acetate,	C_5H_{11}, $C_2H_3O_2$	=	“
Butyl propionate,	C_4H_9, $C_3H_5O_2$	=	“
Propyl butyrate,	C_3H_7, $C_4H_7O_2$	=	“
Ethyl valerate,	C_2H_5, $C_5H_9O_2$	=	“
Methyl caproate,	CH_3, $C_6H_{11}O_2$	=	“

In these ethers the hydrocarbon radicles replace hydrogen-atoms exactly as if they were univalent metals. If the first compound in the column, which is an acid, is treated with a solution of caustic soda, its sodium salt is formed and water is set free. The second compound, similarly treated, would give sodium formate and hexyl alcohol ; the third, sodium acetate and amyl alcohol ; the fourth, sodium propionate and butyl alcohol, etc. So then, although the seven compounds have the same percentage composition and molecular weight, it is easy to demonstrate experimentally that they differ in chemical structure, and to show wherein the differences lie. Some cases of isomerism are less easily explained ; but all are explainable in some such general way.

If from acetic acid, $C_2H_4O_2$, we withdraw a hydroxyl group, OH, a compound radicle called acetyl, C_2H_3O, will remain. This radicle does not exist in the free state, but some of its compounds are interesting. Thus, it forms a chloride, C_2H_3OCl, which is well known, and several *amides*. These resemble the *amines*, with this difference, that whereas in the latter compounds the hydrogen of ammonia is replaced by basic or positive radicles, in the amides the replacement is effected by acid or negative groups. Thus:

$$N\left\{\begin{matrix}C_2H_5\\H\\H\end{matrix}\right.$$

Ethylamine.

$$N\left\{\begin{matrix}C_2H_5\\C_2H_5\\H\end{matrix}\right.$$

Diethylamine.

$$N\left\{\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\end{matrix}\right.$$

Triethylamine.

$$N\left\{\begin{matrix}C_2H_3O\\H\\H\end{matrix}\right.$$

Acetamide.

$$N\left\{\begin{matrix}C_2H_3O\\C_2H_3O\\H\end{matrix}\right.$$

Diacetamide.

$$N\left\{\begin{matrix}C_2H_3O\\C_2H_3O\\C_2H_3O.\end{matrix}\right.$$

Triacetamide.

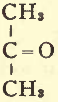
From the other acids of the series, by withdrawal of hydroxyl, other acid radicles are formed; and these have properties similar to acetyl. The amines are all strong bases, the amides are neutral or acid.

By the action of chlorine upon acetic acid, three substitution acids may be obtained. All are strong acids, and yield important derivatives:

$C_2H_4O_2$,	acetic acid.
$C_2H_3ClO_2$,	monochloracetic acid.
$C_2H_2Cl_2O_2$,	dichloracetic "
$C_2HCl_3O_2$,	trichloracetic "

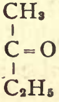
The fourth atom of hydrogen belongs to the COOH group, and, although replaceable by metals, can not be replaced by chlorine. This fact adds to the proof that it is differently combined from the others. Just as aldehyde is related to acetic acid, so also there is a trichloraldehyde related to trichloracetic acid. It is a liquid of formula C_2HCl_3O, and is more briefly known as chloral. It combines with water to form a solid crystalline hydrate which is much used in medicine for producing quiet sleep.

One other compound may be noticed here as the type of an important class. Whenever an acetate is subjected to dry distillation, a volatile liquid called *acetone* is formed. This compound, C_3H_6O, is the first of a large series, members of which may be obtained by a variety of reactions. They are all known as *ketones*, and are structurally formed by the union of two univalent radicles with bivalent carbonyl, CO. Acetone may be called dimethyl-ketone:



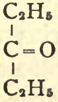
$$\begin{array}{c} CH_3 \\ | \\ C=O \\ | \\ CH_3 \end{array}$$

Dimethyl-ketone.



$$\begin{array}{c} CH_3 \\ | \\ C=O \\ | \\ C_2H_5 \end{array}$$

Ethylmethyl-ketone.



$$\begin{array}{c} C_2H_5 \\ | \\ C=O \\ | \\ C_2H_5 \end{array}$$

Diethyl-ketone.

Etc.

The ketones are isomeric with the aldehydes, but have entirely different constitution.

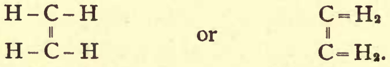
CHAPTER XXXVI.

THE OLEFINES.

THE C_nH_{2n} series of hydrocarbons is known as the olefine series, from "olefiant gas" or ethylene, its first member. Some of its relations to the methane series and to the alcohol radicles are indicated in the following formulæ and the accompanying nomenclature:

C_nH_{2n+2}.	*Alc. radicles.**	C_nH_{2n}.
CH_4, methane.	CH_3, methyl.	CH_2, methylene.*
C_2H_6, ethane.	C_2H_5, ethyl.	C_2H_4, ethylene.
C_3H_8, propane.	C_3H_7, propyl.	C_3H_6, propylene.
C_4H_{10}, butane.	C_4H_9, butyl.	C_4H_8, butylene.
C_5H_{12}, pentane.	C_5H_{11}, amyl.	C_5H_{10}, amylene.
C_6H_{14}, hexane.	C_6H_{13}, hexyl.	C_6H_{12}, hexylene.
C_7H_{16}, heptane.	C_7H_{15}, heptyl.	C_7H_{14}, heptylene.
C_8H_{18}, octane.	C_8H_{17}, octyl.	C_8H_{16}, octylene, etc.

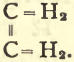
The most important one of these olefines is ethylene, which has already been described as a constituent of coal-gas. In it the two carbon-atoms are united by a double bond of affinity, as shown in the subjoined formula. The second formula is merely a convenient abbreviation of the first.



$$\begin{array}{c} H-C-H \\ \Vert \\ H-C-H \end{array} \quad \text{or} \quad \begin{array}{c} C=H_2 \\ \Vert \\ C=H_2. \end{array}$$

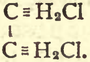
* Known only in compounds; can not exist free.

These olefines all behave as if they were bivalent radicles. Each one unites with two chlorine-atoms to form a chloride, one oxygen-atom to form an oxide, etc. They also take up two hydroxyl groups to form a series of alcohols, which are somewhat better known as glycols. In all these derivatives, however, the carbon-atoms are united by a single bond only, the other bond, which is fixed in the hydrocarbons themselves, being released to new uses. Thus:



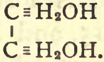
$$\begin{array}{l} C=H_2 \\ \| \\ C=H_2. \end{array}$$

Ethylene.



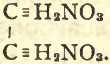
$$\begin{array}{l} C\equiv H_2Cl \\ | \\ C\equiv H_2Cl. \end{array}$$

Ethylene chloride.



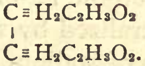
$$\begin{array}{l} C\equiv H_2OH \\ | \\ C\equiv H_2OH. \end{array}$$

Ethylene alcohol.



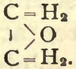
$$\begin{array}{l} C\equiv H_2NO_3 \\ | \\ C\equiv H_2NO_3. \end{array}$$

Ethylene nitrate.



$$\begin{array}{l} C\equiv H_2C_2H_3O_2 \\ | \\ C\equiv H_2C_2H_3O_2. \end{array}$$

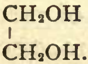
Ethylene acetate.



$$\begin{array}{l} C=H_2 \\ |\;\rangle O \\ C=H_2. \end{array}$$

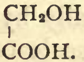
Ethylene oxide.

By the action of oxidizing agents the alcohols of the olefine series, like the alcohols of the methane series, yield acids. Only, instead of a single set of acids, each glycol yields two such derivatives. Thus:



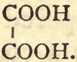
$$\begin{array}{l} CH_2OH \\ | \\ CH_2OH. \end{array}$$

Ethylene alcohol.



$$\begin{array}{l} CH_2OH \\ | \\ COOH. \end{array}$$

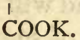
Glycollic acid.



$$\begin{array}{l} COOH \\ | \\ COOH. \end{array}$$

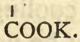
Oxalic acid.

Glycollic acid and its homologues, having but one COOH group, are monobasic; the acids of the oxalic series, on the other hand, are bibasic:



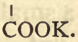
$$\begin{array}{l} CH_2OH \\ | \\ COOK. \end{array}$$

Potassium glycollate.



$$\begin{array}{l} COOH \\ | \\ COOK. \end{array}$$

Hydrogen potassium oxalate.



$$\begin{array}{l} COOK \\ | \\ COOK. \end{array}$$

Neutral potassium oxalate.

Some of these acids and their derivatives are compounds of very great importance. In the glycollic series, for instance, we find lactic acid, which is the acid of sour milk; while from oxalic acid the more important acids of various natural fruits may be rationally derived.

Lactic acid, $C_3H_6O_3$, may be regarded as derived from glycollic acid, $C_2H_4O_3$, by the addition of CH_2. In reality, an atom of hydrogen in glycollic acid is replaced by a methyl group, CH_3. This is equivalent to adding CH_2, and all homologous series, either of hydrocarbons or of their derivatives, are built up by this process of substitution. Lactic acid is a sirupy liquid, having a specific gravity of 1.215, and is easily decomposed by heat. It may be formed synthetically, but it is generally prepared from sour milk. When the latter is used in cookery, the free acid is neutralized by sodium bicarbonate, and a soluble lactate of sodium is produced. Several of the lactates are used medicinally, and all of them are soluble in water. A baking-powder containing lactic acid has recently been patented.

Oxalic acid, $H_2C_2O_4$, is found in the juice of certain plants, such as the sorrel and rhubarb. It may be prepared synthetically by a variety of methods, but on a commercial scale only two processes are used. One of these may be verified experimentally:

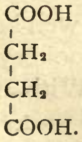
EXPERIMENT 104.—Pour strong nitric acid over a few grammes of white sugar contained in a large flask or beaker. When the action has ceased, and red fumes are no longer given off, evaporate the liquid to a small bulk. On cooling, oxalic acid will crystallize out. Starch may be used instead of sugar.

The second process, which is cheaper, and which of late years has quite supplanted the first, is as follows: When sawdust is heated with caustic potash, potassium oxalate is formed. This, treated with milk of lime, yields an insoluble calcium oxalate. The latter, treated with sulphuric acid, gives calcium sulphate, while oxalic acid is set free, and may be purified by recrystallization.

Oxalic acid is readily soluble, and crystallizes with two molecules of water in prisms which resemble Epsom salt. It is intensely sour, a very strong acid, and quite poisonous. Chalk or magnesia, suspended in water, neutralizes the acid, and is a good antidote in cases of poisoning. In the household, oxalic acid is often used for removing ink-stains or iron-rust from linen or clothing. As, however, the acid attacks the fiber of the cloth, it should be washed out as soon as it has produced the desired bleaching effect. The oxalic acid which was made in Experiment 104 may be used for verifying its solvent property, either upon a rag spotted with ink or upon a sheet of written paper. On a large scale, oxalic acid is used by calico-printers as a means of discharging certain colors.

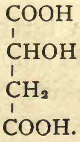
Oxalic acid is the first term of a long homologous series. The second term, malonic acid, $C_3H_4O_4$, is unimportant; but the third member, succinic acid, $C_4H_6O_4$, is interesting. This acid is obtained from amber, and is noteworthy on account of its structural relations to two fruit-acids, malic and tartaric.

Succinic acid, $C_4H_6O_4$.
Malic " $C_4H_6O_5$.
Tartaric " $C_4H_6O_6$.



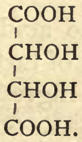
$$\begin{array}{l} COOH \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ COOH. \end{array}$$

Succinic acid.



$$\begin{array}{l} COOH \\ | \\ CHOH \\ | \\ CH_2 \\ | \\ COOH. \end{array}$$

Malic acid.



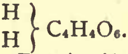
$$\begin{array}{l} COOH \\ | \\ CHOH \\ | \\ CHOH \\ | \\ COOH. \end{array}$$

Tartaric acid.

Malic acid is the acid of apples, pears, and several other fruits and vegetables. It is a white, crystalline body, which may be derived from succinic acid by artificial means, but is more cheaply prepared from mountain-ash berries. Tartaric acid is the acid of grapes, and has considerable practical importance. During the fermentation of wine its potassium salt is deposited in an impure condition on the sides of the wine-casks, and from this crude *tartar* the acid itself may be obtained. It has also been prepared synthetically from succinic acid.

Tartaric acid occurs in white crystals * having an intensely sour taste. It is readily soluble in water, and its solution effervesces strongly with carbonates. In Seidlitz or Rochelle powders it forms the contents of the smaller papers, while the other papers contain a mixture of sodium hydrogen carbonate and a tartrate known as Rochelle salt. The acid is also used in the preparation of a variety of effervescent drinks, and by calico-printers as a discharge for certain mordants.

There are two sets of tartrates, a neutral and an acid series, and some of these salts are practically important. They may be represented in their relations to the acid by condensed formulæ like the following:

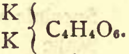


$$\left.\begin{matrix}H\\H\end{matrix}\right\} C_4H_4O_6.$$

Tartaric acid.

$$\left.\begin{matrix}H\\K\end{matrix}\right\} C_4H_4O_6.$$

Hydrogen potassium tartrate.



$$\left.\begin{matrix}K\\K\end{matrix}\right\} C_4H_4O_6.$$

Potassium tartrate.

$$\left.\begin{matrix}K\\Na\end{matrix}\right\} C_4H_4O_6.$$

Rochelle salt.

The acid potassium tartrate is the well-known cream of tartar, which is much used in cookery, and as an ingredient of baking-powders. With a few

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* Commercial tartaric acid occurs oftener as a white powder than it does in the form of crystals.

exceptions, the latter preparations are simply mixtures of cream of tartar with sodium hydrogen carbonate, and when they are acted upon by the moisture of dough, the following reaction takes place:

$$NaHCO_3 + KHC_4H_4O_6 = KNaC_4H_4O_6 + CO_2 + H_2O.$$

The carbonic-acid bubbles, escaping, render the bread or cakes light; the double tartrate, Rochelle salt, remains behind.*

Several other tartrates are used in medicine, and one of them, tartar emetic, is particularly important. It is a double salt containing potassium and antimony, and is commonly represented as containing the latter metal so united with oxygen as to form a univalent radicle $-Sb^{iii}=O$. Upon this basis, tartar emetic would be written, $\left.\begin{matrix}K\\SbO\end{matrix}\right\}C_4H_4O_6$; but recent investigations show that its constitution is more complicated. The salt is a powerful emetic, and in large doses is poisonous.

One other fruit-acid, although not derived from the foregoing acids, may fairly be described here. Citric acid, $C_6H_8O_7$, is found in oranges and lemons, and, with malic acid, in such fruits as the currant and gooseberry. It forms white, soluble crystals, which contain three COOH groups, and therefore three atoms of replaceable hydrogen. Hence it can form various salts, thus:

$$C_6H_5O_7\left\{\begin{matrix}H\\H\\H\end{matrix}\right. \qquad C_6H_5O_7\left\{\begin{matrix}K\\H\\H\end{matrix}\right. \qquad C_6H_5O_7\left\{\begin{matrix}K\\K\\H\end{matrix}\right. \qquad C_6H_5O_7\left\{\begin{matrix}K\\K\\K\end{matrix}\right.$$

Citric acid. Monopotassic citrate. Dipotassic citrate. Tripotassic citrate.

Etc.

---

* Mrs. Richards's little book on "The Chemistry of Cooking and Cleaning" may be profitably read in connection with this and the following chapter.

CHAPTER XXXVII.

GLYCERIN AND THE FATS.

In preceding chapters we have become acquainted with two classes of alcohols, derived from univalent and bivalent hydrocarbon radicles respectively. These alcohols, we have seen, are simply hydroxides, which, though very different in their outward properties, may be compared as to structure with the hydroxides of the metals. Still other series of alcohols are known, some of which correspond to radicles of higher valency; and these we may compare with inorganic hydroxides, thus:

I.	II.	III.	IV.
KOH.	$Ca(OH)_2$.	$Bi(OH)_3$.	$Si(OH)_4$.
CH_3OH.	$C_2H_4(OH)_2$.	$C_3H_5(OH)_3$.	$C_4H_6(OH)_4$.

There is also an alcohol, *mannite*, which is derived from a sexivalent radicle. Its formula is $C_6H_8(OH)_6$; but its description, as well as that of the compound cited in the fourth column above, *erythrite*, must be looked for in some of the larger treatises upon organic chemistry.

The trivalent alcohol $C_3H_5(OH)_3$, or $C_3H_8O_3$, is, however, a body of great practical and theoretical importance. It is commonly known as glycerin;

and from it all the natural fats and fatty oils are systematically derived.

In Chapter XXXV it was shown that when a compound ether is treated with caustic alkalies it is decomposed, an alcohol being set free and an alkaline salt formed. For example, ethyl acetate and caustic soda yield sodium acetate and ethyl alcohol, as follows:

$$C_2H_5C_2H_3O_2 + NaOH = NaC_2H_3O_2 + C_2H_5OH.$$

Now, the natural fats are simply ethers corresponding to glycerin, and they may be decomposed in precisely the same way. If we take stearin, which is a tristearate of glyceryl, C_3H_5, sodium stearate will be formed and stearic acid will be liberated.

$$C_3H_5(C_{18}H_{35}O_2)_3 + 3NaOH = C_3H_5(OH)_3 + 3NaC_{18}H_{35}O_2.$$

This method of decomposition is known as saponification, from the fact that the alkaline salts produced by it are ordinary soaps.

On a large scale, glycerin is prepared either by saponifying a fat or oil with lime or lead oxide, which yield insoluble calcium or lead soaps and set the glycerin free, or else by acting on fats under great pressures with superheated steam. The latter process readily decomposes a fat, and separates it at once into glycerin and an acid in such a way that both products are immediately recoverable. In the preparation of stearic acid this method of decomposition is practically applied, and both glycerin and the acid are saved. The latter is used in the manufacture of candles.*

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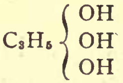
* For details about the stearine industry, see Wagner's "Chemical Technology," pp. 620–636.

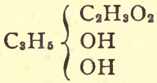
Glycerin is a colorless, sirupy liquid, of specific gravity 1.28. It solidifies at low temperatures, and distills, with partial decomposition, at 275°–280°. It distills more perfectly in a vacuum. It has a very sweet taste, and mixes readily in all proportions with water and alcohol. It has a great variety of uses, as a solvent or as a lubricator, and its household application to chapped lips or hands is universally familiar. With feeble oxidizing agents it yields glyceric acid, $C_3H_6O_4$.

The ethers derived from glycerin are numerous, and, at first sight, complicated. Since the alcohol itself is derived from a trivalent radicle, and has three hydroxyl groups, it follows that with any given monobasic acid it may form at least three derivatives. Thus, with acetic acid, $HC_2H_3O_2$, glycerin yields three ethers, to which are given the names that are written below the subjoined formulæ:



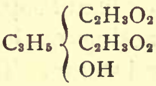
$$C_3H_5\left\{\begin{array}{l}OH\\OH\\OH\end{array}\right.$$

Glycerin.



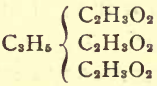
$$C_3H_5\left\{\begin{array}{l}C_2H_3O_2\\OH\\OH\end{array}\right.$$

Monacetin.



$$C_3H_5\left\{\begin{array}{l}C_2H_3O_2\\C_2H_3O_2\\OH\end{array}\right.$$

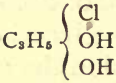
Diacetin.



$$C_3H_5\left\{\begin{array}{l}C_2H_3O_2\\C_2H_3O_2\\C_2H_3O_2\end{array}\right.$$

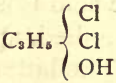
Triacetin.

With hydrochloric acid three compounds are obtained, namely:



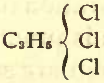
$$C_3H_5\left\{\begin{array}{l}Cl\\OH\\OH\end{array}\right.$$

Chlorhydrin.



$$C_3H_5\left\{\begin{array}{l}Cl\\Cl\\OH\end{array}\right.$$

Dichlorhydrin.



$$C_3H_5\left\{\begin{array}{l}Cl\\Cl\\Cl\end{array}\right.$$

Trichlorhydrin.

In fats and oils we generally encounter the triple ethers of stearic, margaric, palmitic, or oleic acids.

Stearic, margaric, and palmitic acids belong to the regular fatty series, oleic acid stands in another group. Stearic acid is the chief acid in beef-suet, and has the formula $C_{18}H_{36}O_2$; margaric acid is one step lower in the series; and palmitic acid, $C_{16}H_{32}O_2$, is derived both from animal fats and from palm-oil. Oleic acid, $C_{18}H_{34}O_2$, is found in olive-oil and in several other fatty substances. All these fats and oils may be represented by the subjoined formulæ:

$$C_3H_5\left\{\begin{array}{l}C_{16}H_{31}O_2\\C_{16}H_{31}O_2\\C_{16}H_{31}O_2\end{array}\right.\qquad\qquad C_3H_5\left\{\begin{array}{l}C_{17}H_{33}O_2\\C_{17}H_{33}O_2\\C_{17}H_{33}O_2\end{array}\right.$$

Tripalmitin. Trimargarin.

$$C_3H_5\left\{\begin{array}{l}C_{18}H_{35}O_2\\C_{18}H_{35}O_2\\C_{18}H_{35}O_2\end{array}\right.\qquad\qquad C_3H_5\left\{\begin{array}{l}C_{18}H_{33}O_2\\C_{18}H_{33}O_2\\C_{18}H_{33}O_2\end{array}\right.$$

Tristearin. Triolein.

They are commonly called by the briefer names of palmitin, margarin, stearin, and olein, respectively. The more stearin a natural fat contains, the more solid it is; the fluid or pasty fats are richer in olein. Other glycerin ethers are often found, but they need no full description here.

Soap is a mixture of the alkaline salts of the foregoing acids, and is prepared by the direct action of caustic soda or potash upon fats. A soap which contains mostly soda salts and little of the oleate is a hard soap; potash soaps, or soaps containing much oleic acid, are soft soaps. Sometimes, in making cheap soaps, rosin is added; and in some cases, a solution of sodium silicate, or water-glass, is also used. A pure soap is completely soluble in alcohol. All soaps contain a considerable quantity of water.

When glycerin is treated with a mixture of strong nitric and sulphuric acids, an ether is formed which is commonly known as nitroglycerin. This trinitrin, as it is more properly named, is a yellow, oily liquid having the formula $C_3H_5(NO_3)_3$, and possesses extraordinary explosive properties. When kindled by a flame, it burns rather quietly; but when struck by a hammer, or ignited by a percussion-cap, it explodes with terrific violence. This explosion is simply a sudden decomposition, one effect of which is to develop instantaneously a very large volume of gas, in accordance with the following equation:

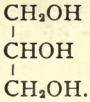
$$4C_3H_5N_3O_9 = 12CO_2 + 12N + 2O + 10H_2O.$$

Dynamite and several other explosive agents much used in blasting are mixtures of nitroglycerin with silica, fine sand, sawdust, or some other solid powder. The oil itself is also used directly as an explosive. Nitroglycerin is a substance which should only be handled with extreme care, for it is not merely explosive but also very poisonous. A single drop placed on the tongue will produce intense headache; and similar discomfort may arise from mere contact of the liquid with the fingers.

When glycerin or any fat is heated to the point at which decomposition begins, acrid vapors are given off. These are produced by a substance called acrolein, the odor of which may be recognized in the unpleasant fumes emitted from the wick of an imperfectly quenched candle. Its formula is C_3H_4O, and it is the aldehyde corresponding to allyl alcohol and acrylic acid. These three compounds are related to each other in the same way as are common alcohol, aldehyde, and acetic acid, as the subjoined formulæ will show:

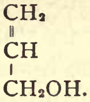
Ethyl alcohol,	C_2H_6O.	Aldehyde,	C_2H_4O.	Acetic acid,	$C_2H_4O_2$.
Allyl "	C_3H_6O.	Acrolein,	C_3H_4O.	Acrylic "	$C_3H_4O_2$.

Allyl alcohol, C_3H_5, OH, is interesting in several ways. It is the hydroxide of a univalent radicle, C_3H_5, which is isomeric with the trivalent radicle of glycerin. These two radicles differ in structure, however, as the following formulæ for the alcohols indicate:



$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH. \end{array}$$

Glycerin.



$$\begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ CH_2OH. \end{array}$$

Allyl alcohol.

A good many derivatives of allyl are known, and some of them are important. Allyl sulphide, $(C_3H_5)_2S$, is the natural oil to which garlic owes its odor; and allyl sulphocyanate, C_3H_5, CNS, is the oil of mustard. The radish, horseradish, etc., also owe their pungency to organic compounds of sulphur.

CHAPTER XXXVIII.

THE CARBOHYDRATES.

In sugar, starch, and a number of allied compounds, the hydrogen and oxygen are combined in just the proportions necessary to form water. By reagents having very strong affinity for water this hydrogen and oxygen may be removed, and charcoal is left behind. For instance, strong sulphuric acid reacts in this manner upon either sugar or starch, as the pupil may easily discover by experiment. Hence the term *carbohydrates*, or hydrates of carbon, has been adopted as a convenient general name for this class of substances, notwithstanding the fact that it is somewhat misleading as to their real chemical structure.

A considerable number of carbohydrates are known, but, as some of them are isomeric with others, all may be classed in three groups under three simple formulæ. These groups are known as the *sucroses*, or sugars proper; the *glucoses;* and the *amyloses*, or starches and gums:

Sucroses.	*Glucoses.*	*Amyloses.*
$C_{12}H_{22}O_{11}$.	$C_6H_{12}O_6$.	$C_6H_{10}O_5$.
Cane-sugar.	Grape-sugar.	Starch.
Milk-sugar.	Levulose.	Dextrin.
Maltose.	Etc.	Gum.
Etc.		Cellulose, etc.

Cane-sugar, or sucrose, $C_{12}H_{22}O_{11}$, is found in the sap of many plants, such as the sugar-cane, sorghum, Indian corn, beet-root, sugar-maple, etc. From all these sources, and perhaps from others, it may be profitably extracted; but sugar-cane is the most important. Beet-root sugar is extensively made in France, and maple-sugar in this country; and the manufacture of sugar from sorghum is an industry which promises great development in the future.*

In the extraction of sugar from sugar-cane the latter is first crushed between heavy iron rollers so as to express the juice. To the latter a little lime is immediately added, to neutralize certain vegetable acids and to precipitate certain fermentable or decomposable impurities. The liquid is next heated to boiling, carefully skimmed, evaporated in copper pans to near the crystallizing point, and filtered through bags of cotton or linen. On cooling, a crystalline mass of moist brown sugar is deposited; and the remaining syrup, upon further evaporation, yields still more. When the second crop of crystals has been removed, a dark, thick molasses, rich in uncrystallized sugar, remains behind. This is either sent into market as it is, or else fermented and distilled into rum.

Brown sugar owes its color to organic impurities, which are removed by the following process of refining: The sugar, dissolved in very little water, is first heated in a copper pan. Albumen, generally in the form of blood, is then added, which, coagulating, carries down the impurities of the sugar in a

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* The United States Department of Agriculture at Washington has issued very valuable reports upon this industry, and also upon the subject of sugar from beets.

sort of dense clot. The liquid is next heated to the boiling-point with a little animal charcoal, and, after running through a charcoal filter, is concentrated to the point of crystallization. This concentration is now generally effected in a vacuum-pan. Finally, the purified sugar is drained of adhering syrup and dried.

Pure sugar is a white, crystalline solid, of specific gravity 1.59. It melts at 160°, forming the amber-colored mass known as barley-candy. At higher temperatures it turns brown, loses water, and is converted into a substance called *caramel*, which is somewhat used for coloring alcoholic liquors. In rock-candy, sugar is highly crystallized; in granulated sugar the crystals are small and separate; in loaf or lump sugar the crystalline character is evident throughout the mass. In all of these forms sugar is easily soluble, and very sweet. If a sample of commercial sugar fails to dissolve completely in hot water, the insoluble residue may be regarded as evidence of adulteration.

Chemically considered, sugar is the alcohol of an octad radicle. Its eight hydroxyl groups may be replaced by eight NO_3 groups, to form an explosive octonitrate, or by eight acetic groups to produce an octoacetate. These derivatives, however, have been incompletely studied.

Lactose, or milk-sugar, is obtained from the whey of milk, and is isomeric with sucrose. It forms hard, white crystals, which grit between the teeth, and are less sweet than cane-sugar. They contain one molecule of water of crystallization, so that their formula is written $C_{12}H_{22}O_{11}, H_2O$. Lactose is used in preparing the little globules of the homœopathic pharmacy. Several other isomers of sucrose and lactose are known.

Cane-sugar itself does not undergo fermentation; but by the action of yeast it is converted into a mixture of two glucoses, both of which ferment readily. In this transformation it takes up one molecule of water, so that the whole change may be written out as follows:

$$C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6.$$

One of these glucoses is termed dextrose or grape-sugar; the other is called levulose or fruit-sugar. The latter is the more readily soluble of the two, and is uncrystallizable. Dextrose, together with sucrose, occurs in many fruits; with levulose it is found in fruits and in honey. Commercial glucose is commonly a mixture of both substances.

On a large scale, glucose is made by the action of very dilute sulphuric acid upon starch.

Experiment 105.—Add one cubic centimetre of strong sulphuric acid to one hundred cubic centimetres of water, and heat in a flask to boiling. Mix ten grammes of starch to a thin paste with water, and pour it very slowly into the acid, so as not to check the boiling. Continue to boil for about three hours, and then add powdered chalk until all free acid has been neutralized. Filter off the insoluble calcium sulphate thus formed, and evaporate the filtrate to the consistency of a thick syrup. The latter will be sweet, and will deposit crystals of dextrose if left standing. By essentially this process immense quantities of glucose are now made from the starch of Indian corn. The product is cheaper than cane-sugar, though less sweet, and is largely used to adulterate sugars and syrups, in the manufacture of candies, by brewers for modifying the quality of beer, and for a variety of other more legitimate purposes.*

Starch, which has the formula $C_6H_{10}O_5$ or some multiple thereof, is found in all grains, in such vegetables as the potato, in unripe fruits, and to a greater or less extent throughout the whole plant-kingdom. Beans, peas, and rice are especially rich in it; sago and tapioca are varieties of it; and, in short, the nutritive value of nearly all vegetables depends in great part upon the amount of starch which they contain. Pure starch is prepared chiefly from wheat-flour or from potatoes. It consists of a white powder made up of microscopic granules (Fig. 53), which are insoluble in water. If heated with water to above 60°, however, they burst, and form the jelly-like starch-paste which is so familiar to the housekeeper. With tincture of iodine starch forms a blue compound; and by this reaction it may be distinguished from all isomers.†

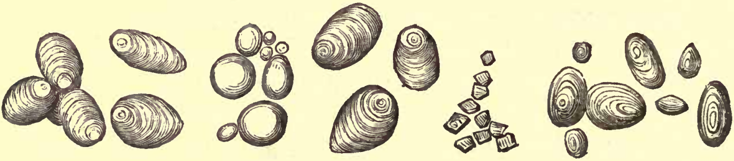

FIG. 53.—Starch Granules, Magnified.

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* The question whether artificial glucose is wholesome or not is still under discussion. At the worst, it is not a dangerous article of diet.

† The pupil may profitably apply this test for starch to flour, rice, bread, potatoes, etc. Boil each article with a little water, and then add a drop of the tincture.

By heating to about 205° starch is converted into an isomeric compound, dextrin. This substance is soluble in water, yielding a gummy solution which is applied to the backs of postage-stamps and used for other similar purposes. Dextrin is largely manufactured under the name of "British gum." Most of the natural gums are isomers of starch and dextrin. Gum-arabic, however, is a mixture of the potassium and calcium salts of arabic acid, $(C_6H_{10}O_5)_2$. Pectin, which is found in most fruits, and which enables their juice to form jellies, is allied to the gums and starches; but its exact character is not yet definitely understood.

Cellulose, $(C_6H_{10}O_5)_3$, is the substance which chiefly constitutes all vegetable fiber. Wood consists mainly of cellulose, and cotton is cellulose practically pure. By sulphuric acid cellulose may be converted into glucose; and the latter may be made from old rags, or even from sawdust.

When cellulose is treated with a mixture of strong nitric and sulphuric acids it is transformed into nitrocellulose or pyroxylin. This compound, $C_6H_7(NO_2)_3O_5$, is commonly known as gun-cotton, and is remarkable for its explosive properties. Outwardly, by the change from cotton to gun-cotton, the vegetable fiber remains the same; and it may be spun into thread, woven into cloth, or made into paper, the same as before. It explodes, however, either by percussion or upon the touch of a flame, more violently than gunpowder; and it is somewhat used as an explosive agent.

Gun-cotton dissolves easily in a mixture of alcohol and ether, forming a solution which is known as collodion. This liquid evaporates rapidly, leaving a film of gun-cotton behind; and it is used for a variety of surgical purposes and for photography. The latter use was described in a previous chapter; its surgical value is due to its power of covering raw or inflamed surfaces, as in the case of scalds and burns, with a sort of artificial skin, and thereby protecting them from contact with the air.*

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* Details concerning many of the bodies described in this chapter may be read up to advantage in Wagner's "Chemical Technology."

CHAPTER XXXIX.

THE BENZENE DERIVATIVES.

BENZENE,* C_6H_6, is a hydrocarbon of remarkable interest. It has been prepared by synthesis from acetylene, C_2H_2, and by several other methods; but it is chiefly obtained from the coal-tar which accumulates in the gas-works. The benzene is purified by several distillations, and forms a colorless liquid, lighter than water, and having a peculiar odor resembling coal-gas. It boils at 80°, and solidifies at 3°. Its vapor, as well as the liquid, are highly inflammable.

Benzene is chiefly useful in the preparation of its derivatives; and these are of the highest importance. They are all derived from benzene by the substitution of other elements or radicles for the hydrogen, while the six carbon-atoms remain as a permanent nucleus. These are supposed to be arranged in the form of a ring or closed chain, each having three bonds of affinity satisfied. Thus, each carbon-atom is still able to hold one hydrogen-atom, as the following diagram will show: †

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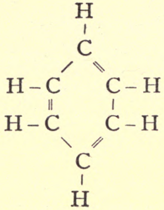
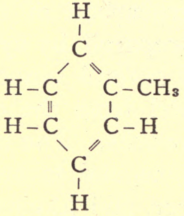
* Often called benz*ol.* The benz*ine* of the shops is usually a mixture of volatile hydrocarbons of the C_nH_{2n+2} series. It is obtained from petroleum, and is very different from benzene proper.

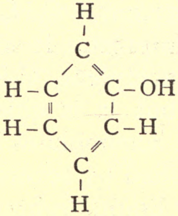
† Other structural formulæ are possible, but this one is the best for present purposes.



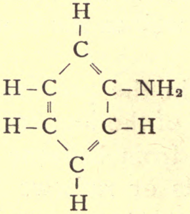
From this formula the formulæ of the derivatives are easily deduced, as a few examples will indicate:



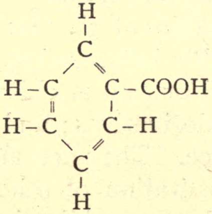
Methyl-benzene, C_7H_8.



Phenol, C_6H_7O.



Aniline, C_6H_7N.



Benzoic acid, $C_7H_6O_2$.

Since every hydrogen-atom in benzene is thus replaceable, the possible number of benzene derivatives is almost infinite. Thousands of them are actually known; hundreds are discovered every year. Only a few of the more striking and useful can be described in this treatise.

Phenol, C_6H_5OH, commonly called carbolic acid,* is a compound of great value as an antiseptic.

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* It is not really an acid.

It is chiefly obtained from coal-tar by a process of distillation, and forms white, deliquescent crystals which melt at 39.5° and boil at 182°. Commercial phenol generally has a reddish tinge, due to impurities. It has a smoky odor and a burning taste, and is much used in medicine and surgery for disinfecting sick-rooms, for preventing gangrene in wounds, etc. It is highly poisonous.

By the action of strong nitric acid upon phenol the latter is converted into trinitrophenol or picric acid, $C_6H_2(NO_2)_3OH$. This substance occurs in yellow, intensely bitter crystals, which are used for giving a yellow color to silk. The picrates are salts which explode violently by percussion, and some of them have been used in gunnery and in submarine torpedoes.

When nitric acid acts on benzene directly, nitrobenzene, $C_6H_5NO_2$, is produced. This is a volatile liquid, having an odor like that of bitter-almonds. Although somewhat poisonous, it is used in the manufacture of cheap flavoring essences and in perfumery. Three isomeric dinitrobenzenes, $C_6H_4(NO_2)_2$, all solid, are also known.

When nitrobenzene is mixed with iron-filings and dilute sulphuric acid, the nascent hydrogen evolved from the two latter substances reduces it to amidobenzene,* or aniline, $C_6H_5NH_2$. This compound is sometimes called phenylamine, the group C_6H_5 being frequently known as phenyl. Aniline is an oily liquid of specific gravity 1.036, which boils at 181°, and has a peculiar, soapy, dis-

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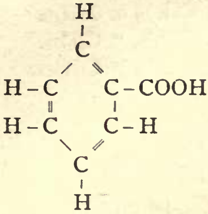
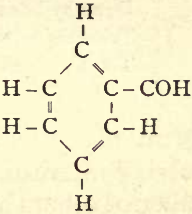
* Compounds containing the group NH_2 are called "amido-compounds." Many other nitro-compounds (containing NO_2) are similarly reducible by hydrogen.

agreeable odor. It is a powerful base, and unites with nearly all acids to form highly crystalline salts. With oxidizing agents it yields a great variety of derivatives; and some of these are among our most valuable and brilliant dyes. Nearly all the gorgeous colors now used in silks and satins are prepared indirectly from the benzene of coal-tar. Some of them are salts of a complex base, rosaniline, $C_{20}H_{19}N_3$; which, though colorless itself, yields compounds of marvelous beauty. For example, rosaniline combines with hydrochloric acid to form the color known as magenta. This substance, in the solid state, forms crystals of a rich, metallic, beetle-green color, which yield with alcohol a solution of a magnificent red. Other reds, purples, violets, yellows, blues, greens, and a very stable black are also found among the derivatives of aniline. Thirty years ago, coal-tar was worthless; today whole industries, giving employment to thousands of men, depend upon it.

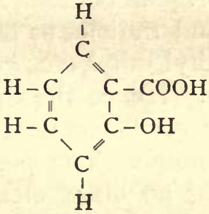
In some of the preceding chapters we have studied the relations of certain alcohols to derivatives known as acids and as aldehydes. In all aldehydes the group $\mathrm{H{-}\underset{|}{C}{=}O}$ occurs, and in all acids we find the more complex group $\mathrm{O{-}H{-}\underset{|}{C}{=}O}$. In each of these groups one carbon bond is free, by means of which other groups can be chemically held in union; and whenever we find in any compound either group, that compound will have the properties of an acid or an aldehyde as the case may be. Among the benzene derivatives we meet many compounds illustrating these principles, and a few formulæ will make the subject clear:



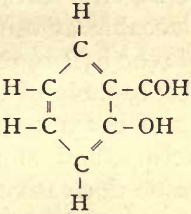
Benzoic acid.



Benzaldehyde.



Salicylic acid.



Salicyl aldehyde.

These substances are of some importance. Benzoic acid is obtained from gum-benzoin, and is of some use in medicine; benzaldehyde is the well-known fragrant oil of bitter-almonds; salicyl aldehyde is the odoriferous principle of the meadow-sweet spiræa; and salicylic acid, which is now made synthetically from phenol, is a very important remedy in the treatment of rheumatic disorders. Sodium salicylate is often used instead of the acid. Methyl salicylate is the natural oil of the wintergreen or checkerberry.

When the hydrogen of benzene is replaced by a radicle of the methyl series, new hydrocarbons, homologous with benzene itself, are produced. Thus, for example, we have:

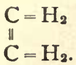
Benzene,	C_6H_6.	
Methylbenzene,	$C_6H_5CH_3$,	or C_7H_8.
Ethylbenzene,	$C_6H_5C_2H_5$,	" C_8H_{10}.
Propylbenzene,	$C_6H_5C_3H_7$,	" C_9H_{12}.

Dimethylbenzene,	$C_6H_4(CH_3)_2$, or C_8H_{10}.
Trimethylbenzene,	$C_6H_3(CH_3)_3$, " C_9H_{12}.
Tetramethylbenzene,	$C_6H_2(CH_3)_4$, " $C_{10}H_{14}$.
	etc.

A great many of these hydrocarbons are known, involving interesting cases of isomerism ; and a vast number of others are possible. In each of them the unreplaced hydrogen of the original benzene is still replaceable by other atoms and radicles as before, while the hydrogen of the methyl, ethyl, etc., groups is also capable of substitution. Hence the derivatives of these compounds are very complicated in structure, and almost innumerable. The possible benzene derivatives, containing no other elements than carbon, hydrogen, oxygen, and nitrogen, would have to be counted by millions.

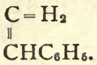
Next to benzene, methyl benzene or *toluene*, $C_6H_5CH_3$, is the most important hydrocarbon of the series. With nitric acid it yields nitrotoluene, $C_6H_4NO_2CH_3$, which is easily reduced by nascent hydrogen to amido-toluene, $C_6H_4NH_2CH_3$, a compound which is more commonly known as toluidine. This substance occurs to some extent in commercial aniline, and it plays an essential part in the formation of the aniline dyes.

We have already noticed that benzene, minus one atom of hydrogen, may behave like a univalent radicle, and that this group, C_6H_5, is sometimes known as phenyl. Now, phenyl may replace one hydrogen-atom in ethylene, C_2H_4, yielding a hydrocarbon called phenylethylene, or cinnamene, $C_2H_3C_6H_5$. From this hydrocarbon other compounds may be in turn derived, and two of these are noteworthy :



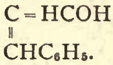
$$\begin{array}{l} C=H_2 \\ \Vert \\ C=H_2. \end{array}$$

Ethylene.



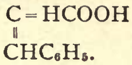
$$\begin{array}{l} C=H_2 \\ \Vert \\ CHC_6H_5. \end{array}$$

Cinnamene.



$$\begin{array}{l} C=HCOH \\ \Vert \\ CHC_6H_5. \end{array}$$

Cinnamic aldehyde.

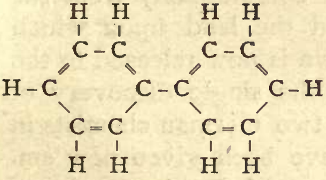


$$\begin{array}{l} C=HCOOH \\ \Vert \\ CHC_6H_5. \end{array}$$

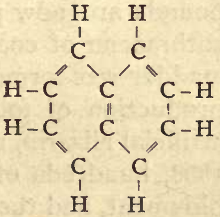
Cinnamic acid.

Cinnamic aldehyde, C_9H_8O, is the chief constituent of the fragrant oil of cinnamon; and from cinnamic acid, by a series of synthetic processes, indigo has been obtained. Indigo originally was prepared from the leaves and stems of the indigo-plant, which, covered with water and allowed to ferment, gradually yielded this valuable coloring-matter. When absolutely pure its formula is $C_{16}H_{10}N_2O_2$; and it is probable that in the near future it will be largely made artificially from among the hydrocarbon products of coal-tar.* Even at the date of writing, artificial indigo is being produced in Germany upon a commercial scale.

In addition to the great number of hydrocarbons derivable from benzene by the substitution of hydrogen, still others, even more complicated, are formed by the combination of two or more benzene rings with each other. A few formulæ will illustrate this matter:



Diphenyl, $C_{12}H_{10}$.



Naphthalene, $C_{10}H_8$.

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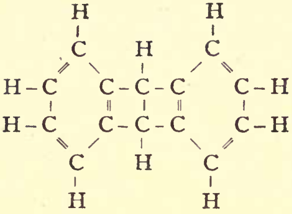
* Full details concerning the synthesis of indigo would be too complicated for introduction in a school text-book. For such matters the larger treatises upon organic chemistry may be consulted. Strecker's treatise is good.



Anthracene, $C_{14}H_{10}$.

From all such hydrocarbons as these a vast number of complicated derivatives may be obtained, and some of them have great practical importance. Naphthalene and anthracene are both white solids, obtained from coal-tar oil, and from each some useful dye-stuffs may be prepared. Thus, from naphthalene we get naphthalene-yellow, $C_{10}H_5OH(NO_2)_2$, and, from anthracene, alizarin and purpurin are artificially obtained. These latter substances are found, naturally, in the madder-root, which has been used from time immemorial as a red dye, and which was cultivated over large areas in Europe. The familiar Turkey-red is simply the color produced by madder. Alizarin has the formula $C_{14}H_8O_4$, and purpurin is $C_{14}H_8O_5$. Both compounds are now prepared commercially from the anthracene of coal-tar, and the land upon which madder was formerly grown is now released to the production of food. By the single discovery of artificial alizarin, made by two German chemists in 1868, hundreds of men have been given new employment, and the world's wealth has been perceptibly increased.

Enough has been said to illustrate the general principles which govern the formation of the derivatives of benzene. By a careful study of the benzene ring, chemists are now able to predict the existence of compounds in advance of actual discovery, and to plan available methods for their production. Alizarin, for example, was thus obtained—not by accident, but by a deliberate application of principles with skill and foresight. Plainly, then, the consideration of the structural formulæ, to which this chapter has been so largely devoted, is not by any means a useless exercise of the imagination. The formulæ may be capable of future improvement, but, as they now stand, they are of great use in the development of chemical science.

CHAPTER XL.

THE TERPENES, CAMPHORS, ALKALOIDS, AND GLUCOSIDES.

THE substances described in this chapter are all products of plant-life. Some of them are structurally related to benzene, but for the greater number the structure is as yet undetermined.

The *terpenes* are a class of volatile hydrocarbons of the general formula $C_{10}H_{16}$. Most of them occur as the so-called "essential oils" of plants; and, although they are isomeric, they differ widely in their external properties. The oils of lemon, orange, bergamot, lavender, pepper, etc., are examples. There are many others, and compounds containing oxygen are often mixed with them.

In common turpentine, which exudes from cuts made in the bark of several species of pine, we have a mixture of terpenes. When it is distilled with water, oil of turpentine, $C_{10}H_{16}$, distills over, and rosin remains in the retort. The oil has a specific gravity of 0.86, and boils at 161°. The rosin contains oxygen, and consists in great part of sylvic acid, $C_{20}H_{30}O_2$. In structure the terpenes are undoubtedly allied to the benzene series, but the causes of isomerism remain to be made out. That substances so different as turpentine, oil of orange-flowers, and oil of pepper, should have the same percentage composition, is certainly remarkable.

The *camphors* are closely related to the terpenes, but contain oxygen. Ordinary camphor, which is the best example, is a white solid, having the formula $C_{10}H_{16}O$. It melts at 175°, boils at 204°, and has a peculiar, characteristic odor. Nitric acid oxidizes it to camphoric acid, $C_{10}H_{16}O_4$.

In a great many plants, especially among those which possess marked poisonous properties or medicinal value, are found a class of compounds which are termed *alkaloids*. Of these a few, containing only carbon, hydrogen, and nitrogen, are liquids; the others, which contain oxygen also, are crystallizable solids. They are all bases, and unite with acids to form perfectly definite, well-characterized salts. Only a few of them can be noted here.

Of the liquid alkaloids, conine, $C_8H_{15}N$, and nicotine, $C_{10}H_{14}N_2$, are the most noteworthy. Conine is the active principle of the poison-hemlock (*Conium maculatum*), and nicotine is contained in tobacco. Nicotine is an oily liquid, of a disagreeable odor, and is violently poisonous. Tobacco contains from two to eight per cent of it; but, in smoking, the alkaloid is partly decomposed.

In tea and coffee we find a remarkable solid alkaloid, to which the stimulating effects of these articles are due. This alkaloid, caffeine, $C_8H_{10}N_4O_2$, crystallizes in silky needles, which melt at 178° and sublime at higher temperatures. It is found also in the leaves of the *Ilex Paraguayensis*, or Paraguay tea, and in the drug known as *guarana*. It is a curious fact that widely separated nations should select as stimulants plants which belong to different genera and yet depend upon the same alkaloid for their activity. In cocoa, theobromine, $C_7H_8N_4O_2$, is found. Caffeine is theobromine with one hydrogen-atom replaced by a methyl group.

In opium, which is extracted from certain species of poppy, at least fifteen different alkaloids are found. Some of these occur in very small quantity and are unimportant, but the following are noteworthy:

Morphine, $C_{17}H_{19}NO_3$.
Codeine, $C_{18}H_{21}NO_3$.
Thebaine, $C_{19}H_{21}NO_3$.
Narcotine, $C_{22}H_{23}NO_7$.

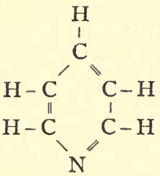
With the alkaloids of opium, meconic acid, $C_7H_4O_7$, is combined. All of these alkaloids are useful in medicine, and all form bitter crystals; all are poisonous, thebaine being the most so. Morphine is chiefly used as sulphate, and is invaluable for quieting pain. Heated under pressure with hydrochloric acid it yields a new base, apomorphine, $C_{17}H_{17}NO_2$, which is a violent emetic. Codeine is methyl-morphine, $C_{17}H_{18}(CH_3)NO_3$.

Cinchona, or Peruvian bark, is another drug containing a remarkable group of alkaloids. The trees which yield it grow wild in the mountainous regions of Peru and Ecuador, and are extensively cultivated in Java and India. Quinine, $C_{20}H_{24}N_2O_2$, and cinchonine, $C_{20}H_{24}N_2O$, are the most important of its constituents. Both alkaloids are valuable remedies in the treatment of fevers, although the first named far surpasses the other. It is intensely bitter, and is administered chiefly as sulphate.

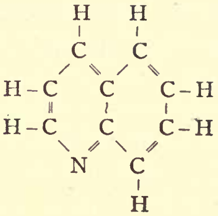
EXPERIMENT 106.—Dissolve in water, with the aid of a drop of weak sulphuric acid, a little quinine sulphate. The solution will be colorless by transmitted light, but with a reflected ray will appear of a delicate, misty blue. This color does not exist in the substance itself, but is produced by its action upon the invisible rays of the spectrum beyond the violet. The property of producing a color in this peculiar way is termed *fluorescence*. The colorless æsculin, from horse-chestnuts, similarly fluoresces with a brilliant blue, uranium compounds fluoresce with a greenish yellow, etc. The phenomenon is beautiful, and not uncommon.

A number of other alkaloids are important, but space permits only the barest mention of them here. In the *nux vomica* two bases exist—namely, strychnine, $C_{21}H_{22}N_2O_2$, and brucine, $C_{23}H_{26}N_2O_4, 4H_2O$. Both are violent poisons, and both are used in small doses medicinally. Aconitine, from aconite; atropine, from belladonna; hyoscyamine, and solanine, are all interesting. Their names are sometimes made to terminate in *ia* instead of *ine*, as atropia, morphia, quinia, strychnia, etc. The termination is only a matter of preference.

Although the chemical structure of the alkaloids has not yet been definitely made out, chemists are progressing rapidly toward a solution of the problem. Doubtless, within a few years, most of these bases will be prepared by synthesis. At present, the following points seem to be clear. In bone-oil, produced by the distillation of bones, a series of bases are found, of which pyridine, C_5H_5N, is the first member. By the destructive distillation of certain alkaloids, another base, chinoline, is formed; and this compound, C_9H_7N, is closely allied to pyridine, as the subjoined formulæ will show:



Pyridine.



Chinoline.

From these bases and their allied compounds the alkaloids are in all probability derived, by a system of hydrogen substitutions like that which serves to explain the derivatives of benzene. The similarity between pyridine and benzene, as regards structure, is evident at a glance; while chinoline is comparable with naphthalene.

Of the *glucosides*, although many are known, but little need be said. These compounds exist in many plants; and by the action of certain ferments they are decomposed into glucose and other bodies which are in general derivatives of benzene. The ferments above mentioned are complex substances, of which the exact composition remains to be determined. The manner in which they act is also little understood. The following glucosides are important:

Salicin, $C_{13}H_{18}O_7$, is found in the bark of willows and poplars. It forms colorless, bitter crystals, which are easily split up by soluble ferments into glucose and saligenin, $C_7H_8O_2$.

$$C_{13}H_{18}O_7 + H_2O = C_7H_8O_2 + C_6H_{12}O_6.$$

Amygdalin, $C_{20}H_{27}NO_{11}$, is the crystallizable bitter principle of bitter-almonds. The latter also contain a ferment called emulsin, and, when they are crushed, the latter converts the amygdalin into benzaldehyde (bitter-almond oil), hydrocyanic acid, and glucose.

$$C_{20}H_{27}NO_{11} + 2H_2O = C_7H_6O + HCN + 2C_6H_{12}O_6.$$

The oil of bitter-almonds does not exist in the perfect fruit, but is formed entirely by this reaction. In the equation the emulsin does not appear.

In the cambium layer of coniferous trees, coniferine, $C_{16}H_{22}O_8$, is found. This, with a ferment, yields glucose, and coniferyl alcohol, $C_{10}H_{12}O_3$. The latter, upon oxidation, is converted into aldehyde and vanilline, $C_8H_8O_3$. Vanilline is the fragrant principle of vanilla-beans, although it may now be made artificially from the coniferine of pine-trees. Structurally, it is a derivative of benzene.

Populin, $C_{20}H_{22}O_8$, from the aspen-tree; fraxin, $C_{27}H_{30}O_{17}$, from the bark of the ash; phloridzin, $C_{21}H_{24}O_{10}$, from various fruit-trees; and æsculin, $C_{21}H_{24}O_{13}$, from the horse-chestnut, are other common glucosides. There are also a group of these compounds derived from oak-bark, nut-galls, etc., which are known as the tannic acids or tannins. These compounds all have an astringent taste, and yield black precipitates with salts of iron; they also act upon the animal membranes (as, for example, the skin) forming leather. Probably they all contain the true tannic acid, $C_{14}H_{10}O_9$, which is simply derived from gallic acid, $C_7H_6O_5$, a derivative of benzene:

$$C_7H_6O_5 = C_6H_2(OH)_3COOH.$$

Tannin and gallic acid are both used in the manufacture of ink.

CHAPTER XLI.

ANIMAL CHEMISTRY.—FERMENTATION.

WHEN we study the compounds produced by animal life, although we have but few elements to consider, we meet with compounds of the very greatest complexity. As a rule, subject to some exceptions, they contain carbon, hydrogen, oxygen, and nitrogen, and are uncrystallizable. Some of them contain sulphur or phosphorus, and, except in a few cases, we know little or nothing as to their chemical structure.

Two groups of these compounds are especially important, inasmuch as, together with water, fat, and the earthy matter of the bones, they make up the greater part of every higher animal organism. These other substances we have already considered, and we may now devote our attention to the two groups in question, the albuminoids and the gelatins.

The albuminoids are a class of substances which are best represented by the following compounds. They all putrefy easily, coagulate or form clots upon heating or by contact with alcohol, and are soluble either in water or dilute hydrochloric acid.

Albumen, the chief compound of the group, is found, dissolved in water, in the whites of eggs and the serum of blood. The change from fluid to solid white, when an egg is boiled, illustrates the coagulation by heat above referred to. When perfectly freed from water, albumen is a yellowish, transparent solid, having a composition which is tolerably well represented by the formula $C_{72}H_{112}N_{18}SO_{22}$. A similar compound, not identical, however, is found in all vegetable juices. It is called vegetable albumen.

EXPERIMENT 107. — Divide the white of an egg into three portions, and put them into three different test-tubes. Heat one, and add to the others a little alcohol and an aqueous solution of mercuric chloride respectively. In each case coagulation will ensue. Repeat the experiment, if convenient, with a little blood. One drop of the latter in each test-tube will suffice.

In blood, with albumen, are found two other albuminoids, which so react upon each other as to form a third substance, called fibrin. The latter separates from blood very soon after the latter has left the body, and forms the solid clot. The albumen remains behind in the liquid serum. Fibrin is best obtained by heating fresh blood until a clot is produced, and washing the latter thoroughly under a stream of water. It forms a mass of whitish or grayish fibers. Blood also contains a crystallizable coloring-matter, called hæmoglobin. The latter decomposes easily into an albuminoid, and a body called hematin, which contains iron. Its probable formula is $C_{34}H_{34}N_4FeO_5$.

Casein, the albuminoid constituent of milk and cheese, separates in curds whenever milk becomes sour. With it, milk contains water, fat (or butter), milk-sugar, sodium chloride, calcium phosphate, etc. The casein is held in solution by a little alkali, and may be precipitated by acids. Gluten and legumin are vegetable caseins.

In most foods the albuminoids play an important part. When they are taken into the stomach they first dissolve in the weak hydrochloric and lactic acids of the gastric juice. The latter fluid also contains a peculiar ferment, called pepsin, which rapidly converts the albuminoids into substances known as peptones, and these, unlike albumen itself, are capable of diffusion through membranes. These chemical changes are essential to digestion, and to the absorption of the valuable constituents of the food into the system. All the albuminoids dissolve in very dilute hydrochloric acid (one part of acid in a thousand of water) to form acid albumen or syntonin. This substance does not coagulate upon heating, and from its solution alkalies reprecipitate albumen.

The gelatins, of which common gelatin is the best example, are obtained from bone, cartilage, connective tissue, etc. Common gelatin occurs in commerce in sheets, which vary in color according to purity. The finest qualities, made from the "sounds" of certain fishes, are used for making jellies; the coarser grades form glue. Gelatin is also valuable in various photographic processes, in making hektograph plates, and for many other purposes. It dissolves in hot water, and sets to a jelly on cooling. By tannin it is precipitated from its solutions, and the formation of leather is due to the action of the tannin of the tan-bark upon the gelatinous matter of skins. Chondrin is a peculiar form of gelatin obtained from rib cartilage. It is precipitated from solution by nearly all acids, whereas ordinary gelatin is not.

As might be naturally inferred from their great complexity, the albuminoids and gelatins are very unstable. Their unwieldy molecules tend to split up into simpler groups of atoms; and in the process of putrefaction they are the compounds which are first and most affected. Putrefaction, however, is but a special kind of fermentation; and this set of phenomena we may now profitably consider.

Whenever the juice of fruits, such as grapes or apples, is freely exposed to the air, a series of changes occur which end in the formation of alcohol. If the latter be left to itself, a further change takes place, and vinegar is produced. Similar reactions are noticed when yeast is allowed to act upon starch or sugar, when milk turns sour or butter becomes rancid, and all of them are ascribed to fermentation. All of them are due to the action of minute living organisms, microscopic plants or animals, and of these the germs are found nearly everywhere. The latter may be killed by extreme cold or extreme heat, and no true fermentation can occur in bodies from which they are excluded. Milk, fruit, meats, vegetables, fish, etc., heated to boiling and sealed up in air-tight tin cans, may be kept for years without alteration; but, when they are exposed to air containing ferment-germs, fermentation and putrefaction speedily ensue. Antiseptics, such as salt, phenol, alcohol, etc., owe their power of preventing decay to the fact that they kill all germs of ferments; and ice acts as a preservative by chilling them below the temperatures at which they are capable of activity. Many contagious diseases, such as small-pox, typhoid fever, etc., are also ascribed to similar germs, which, when inhaled, set up processes of fermentation in the living body; and disinfectants are used in the sick-room for the direct purpose of destroying these dangerous creatures. Our knowledge of them is as yet in its infancy, but new discoveries are being made almost daily; and we may reasonably hope that in a few years many important advances will be accomplished.

In putrefaction, the changes which the albuminoids undergo are so complex as to be outside the range of an elementary treatise. The following kinds of fermentation are simpler:

1. Alcoholic fermentation. The glucoses, when exposed to the action of the yeast-plant, undergo fermentation, yielding large quantities of carbon dioxide and alcohol. Traces of succinic acid and glycerin are formed at the same time. Sugar and starch have first to be transformed into glucoses before fermentation can take place. In brewing, the starch of the grain is converted into glucose by a peculiar substance called diastase, which is formed in the process of malting. Although this fermentation produces alcohol, an excess of alcohol will stop it.

2. Acetous fermentation. This produces acetic acid, and is noticed when wine, cider, beer-mash, etc., are transformed into vinegar. When vinegar is made by allowing alcohol to trickle over wood-shavings, the latter carry the ferment-germs upon their surfaces.

3. Lactic fermentation. This occurs when milk turns sour, and results in the formation of lactic acid.

4. Butyric fermentation. This yields butyric acid, and is observed in rancid butter and putrefying cheese.

5. Mucous fermentation, which produces gum and mannite.

6. Nitric fermentation, recently discovered, by which living organisms decompose nitrates, setting nitrogen dioxide free.

For a full discussion of the subject of fermentation, Schützenberger's little treatise may profitably be consulted.*

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* "On Fermentations." No. 20 of the "International Scientific Series."

APPENDIX I.

COMPARATIVE TABLE OF ENGLISH AND METRIC MEASURES.

A. Measures of Length.

Standard unit, one metre.

1 kilometre = 1,000 metres.
1 hectometre = 100 “
1 decametre = 10 “

1 decimetre = 0.100 metre.
1 centimetre = 0.010 “
1 millimetre = 0.001 “

1 metre = 39.37079 inches.
1 decimetre = 3.93708 “
1 centimetre = 0.39371 “
1 millimetre = 0.03937 “

1 inch = 2.53995 centimetres.
1 foot = 3.04794 decimetres.
1 yard = 0.914383 metre.
1 mile = 1.609315 kilometres.

B. Measures of Surface.

1 sq. metre = 10.7643 sq. feet.
1 sq. centimetre = 0.1550 sq. inch.
1 sq. millimetre = 0.0015 sq. inch.

1 sq. foot = 9.28997 sq. dm.
1 sq. inch = 6.45137 sq. cm.
1 sq. yard = 0.8361 sq. m.

C. Measures of Volume.

1 litre = 1 cubic decimetre.
1 “ = 1,000 “ centimetres.

1 litre = 61.02705 cu. inches.
1 cu. cm. = 0.06103 cu. inch.
1 litre = 1.05672 U. S. qts.

1 cu. inch = 16.38618 cu. cm.
1 cu. foot = 28.31531 cu. dm.
1 U. S. qt. = 0.9469 litre.

D. Measures of Weight.

The unit, one gramme, is the weight of one cubic centimetre of distilled water, at the temperature of 4° C.

1 kilogramme = 1,000 grs.
1 hectogramme = 100 "
1 decagramme = 10 "

1 decigramme = 0.1000 gr.
1 centigramme = 0.0100 "
1 milligramme = 0.0010 "

1 kilogr. = 2.204621 lb. avoir.
1 " = 32.15073 oz. troy.
1 gr. = 15.43235 grains.

1 grain = 64.799 milligr.
1 oz. troy = 31.1035 gr.
1 lb. avoir. = 0.45359 kilogr.

One thousand kilogrammes vary but little from the "long" ton of 2,240 pounds avoirdupois (0.984206 ton).

The pound avoirdupois contains 7,000 grains.

The same figures which represent the specific gravity of any solid or liquid, referred to water as unity, also represent the weight of one cubic centimetre of the substance, expressed in grammes.

THERMOMETRIC RULES.

To reduce a Fahrenheit temperature to its equivalent in centigrade degrees: Subtract 32°, and multiply the remainder by $\frac{5}{9}$.

To reduce a centigrade temperature to its Fahrenheit equivalent: Multiply by $\frac{9}{5}$, and add 32° to the product.

APPENDIX II.

QUESTIONS AND EXERCISES.

To be amplified or increased at the discretion of the teacher.

CHAPTER I.—1. How do chemical and physical changes differ? 2. Give an example of chemical combination. 3. Give an example of chemical decomposition. 4. Give some points of connection between heat and chemical change. 5. What points must be considered in the complete study of a chemical change? 6. What is understood by *matter?* What by *force?* 7. Is either matter or force destructible? 8. Define chemistry. 9. Name some useful applications of chemistry.

CHAPTER II.—1. Explain what is meant by analysis and synthesis. 2. Define elements and compounds. 3. Which of the following substances are elements? Iron, oxygen, water, air, copper, wood, salt, carbon, sugar, tin, iodine. 4. Explain what is meant by a molecule. 5. What is an atom? 6. What is a *mass* of matter? 7. From what evidence do you infer the existence of atoms and molecules?

CHAPTER III.—1. Describe three methods for the preparation of hydrogen. 2. How does hydrogen occur in nature? 3. Describe the hydrogen-flame. What precaution must be observed in kindling it? 4. What compound is formed by the combustion of hydrogen? 5. What substances are heavier than hydrogen? What does one litre of hydrogen weigh? 6. What law governs the expansion of gases by heat? 7. How does the volume of a gas vary with pressure? 8. What pressure and what temperature are taken as standards of comparison? 9. Given one litre of gas at 0°, what will it become at 37°? What at 83°? What at 273°? 10. Seventy-two volumes of hydrogen are measured at 16°, what will they measure after cooling to 0°? What at —273°? 11. Given ten litres of a gas at 22° and 748 millimetres pressure, what will the volume be at 0° and 760 millimetres? 12. How may gases be liquefied? 13. What are the more important properties of hydrogen? 14. Is hydrogen a metal or a non-metal?

CHAPTER IV.—1. How does oxygen occur in nature? 2. How is oxygen best prepared? What precautions are essential? 3. What are the chief properties of oxygen? 4. Define oxidation. What is an oxide? 5. Is oxygen necessary to combustion? 6. Is oxygen essential to respiration? 7. Wherein is the solubility of oxygen in water important? 8. What is ozone? Describe its properties. 9. What does a litre of oxygen weigh? 10. What volume will 87 grammes of oxygen occupy at 15° and 774 millimetres pressure? 11. What will be the weight of 17 litres of oxygen, measured at 12° and 755 millimetres?

CHAPTER V.—1. What oxides does hydrogen form? 2. What happens when a mixture of oxygen and hydrogen is kindled? 3. How much heat is developed by the combustion of hydrogen? Does any other chemical change develop more heat? 4. Explain the compound blow-pipe. What are its uses? 5. Describe the electrolysis of water. 6. Describe the synthesis of water. 7. In what proportions, by volume and by weight, do oxygen and hydrogen combine to form water? 8. Suppose thirty-six volumes of oxygen and hydrogen unite, what volume will be occupied by the resulting steam? 9. What weight of oxygen would be contained in one gramme of liquid water? What volume would it occupy at 0° and 760 millimetres? 10. Given ten litres of water of 0°, how much steam will it give at 100°? What volume of hydrogen can be obtained from that steam? What weight of hydrogen? 11. What are the chief properties of water? 12. How does water behave upon solidifying? 13. Define a gramme. A litre. A kilogramme. 14. Describe the centigrade and Fahrenheit scales. 15. How may impure water be purified? 16. What is water of crystallization? Define deliquescence and efflorescence.

CHAPTER VI.—1. How does nitrogen occur in nature? 2. How may nitrogen be prepared? 3. What is the composition of the atmosphere? Does it vary in any way? 4. Describe the chief properties of nitrogen. 5. What is the weight of one litre of nitrogen, at 0° and 760 millimetres? 6. What is the weight of 7.33 litres of air, measured at 22° and 758 millimetres?

CHAPTER VII.—1. Describe ammonia gas. What is its exact composition? 2. What is *aqua ammonia?* 3. Name the oxides of nitrogen. 4. Describe nitric acid. What is a nitrate? 5. What action has nitric acids on metals? 6. Define "acid" and "alkali." 7. What are salts and bases? 8. Explain the names nitrous and nitric. 9.

Give the law of definite proportions. 10. Give the law of multiple proportions. Illustrate it. 11. Describe nitrous oxide and its uses. 12. Describe nitrogen dioxide and nitrogen tetroxide.

CHAPTER VIII.—1. What is a chemical symbol? Give examples. 2. Explain the combining weights of oxygen and nitrogen. 3. Explain the combining weights of Cl, Br, I, K, Na, and Ag. 4. State the atomic theory, and explain what is meant by atomic weight. 5. Give and explain the formulæ of several compounds. 6. What weight of oxygen can be prepared from sixty grammes of $KClO_3$? What volume, measured at 10° and 740 millimetres? 7. Explain this equation: $Fe + H_2SO_4 = H_2 + FeSO_4$. What weights of iron and of sulphuric acid would be needed to give fifty grammes of hydrogen? 8. Sixty-five litres of oxygen are wanted, at 27° and 750 millimetres; what weight of $KClO_3$ must be used?

CHAPTER IX.—1. Describe the different forms of carbon. 2. What are the uses of graphite? 3. What are the uses of amorphous carbon? 4. How does charcoal affect coloring-matters? How does it act as a disinfectant? 5. What is coal? 6. Describe methane. 7. What is ordinary coal-gas? 8. Describe a gas-flame. A candle-flame. 9. What is a Bunsen-burner? 10. Describe the mouth blow-pipe and its uses. 11. Explain the safety-lamp.

CHAPTER X.—1. Describe carbon monoxide. 2. What compound is formed when charcoal burns? 3. How do you test for carbon dioxide? 4. How is CO_2 best prepared? 5. What percentage of CO_2 can be obtained from $CaCO_3$? 6. How does CO_2 affect combustion and respiration? 7. Given a kilogramme of limestone, what volume of CO_2 will it yield, measured at 21° and 762 millimetres? 8. How is the atmosphere affected by plants and animals? 9. What is cyanogen? 10. Define a compound radicle. 11. What volume of oxygen would be required for the complete combustion of ten grammes of charcoal? What weight of CO_2 would be produced?

CHAPTER XI.—1. How is the density of carbon-vapor determined? 2. State the two-volume law. 3. Why should the formulæ CH and CN be doubled? 4. Why should the formulæ N_2O_2 and N_2O_4 be halved? 5. What is the vapor density of C_2H_6O? of C_6H_6? of C_6H_7N? 6. State Avogadro's law. 7. How many atoms are there in most elementary molecules? 8. Explain the formula of ozone.

CHAPTER XII.—1. Define valency. 2. In what proportion can two monads combine? Two dyads? A dyad and a monad? A dyad and a triad? A dyad and a tetrad? 3. What valency has the metal in each of the following formulæ? $ZnBr_2$. SbH_3. $AuCl_3$. CdO. ThO_2. $TiCl_4$. Al_2O_3. WCl_6. $BaCO_3$. Ag_2CO_3. $RbNO_3$. $Fe(NO_3)_2$.

4. What is meant by a structural formula? Give examples. 5. What is an unsaturated compound? 6. Explain the valency of cyanogen.

CHAPTER XIII.—1. What elements form the chlorine group? How are they related? What are their atomic weights? 2. Describe hydrofluoric acid. 3. How is chlorine best prepared? 4. What are the properties and uses of chlorine? 5. How does chlorine act as a bleacher or disinfectant? 6. How is hydrochloric acid prepared? Describe it. 7. What weight of HCl can be made from one kilogramme of NaCl? How much H_2SO_4 would be used? What volume would the HCl occupy at 17° and 771 millimetres? 8. What action has hydrochloric acid upon metals? What salts are thereby formed? 9. Describe *aqua regia.*

CHAPTER XIV.—1. Write the formulæ of the oxides and acids of chlorine. Explain their names. 2. What hypochlorites are useful, and why? 3. What are the properties and uses of the chlorates? 4. Describe bromine. What is its vapor density? 5. Describe iodine. 6. What is a convenient test for iodine? 7. Describe the chloride and iodide of nitrogen.

CHAPTER XV.—1. Point out the similarities between O, S, Se, and Te. 2. Describe sulphur. What is the character of its molecule? 3. Describe H_2S. What volume of H_2S at 0° and 760 millimetres could be evolved from 50 grammes of FeS? 4. What weight of water and of SO_2 would be formed by the combination of one litre of H_2S. 5. Explain, with equations, the precipitation of some metallic salts by H_2S. 6. Which is the most important oxide of sulphur? What are its properties and uses? 7. Define the term *anhydride.* How do the anhydrides form acids?

CHAPTER XVI.—1. Give the names and formulæ of the sulphur acids. 2. Explain the manufacture of H_2SO_4, and write the equations. 3. State some uses of sulphuric acid. What is its action upon ordinary organic matter? 4. What is Nordhausen acid? 5. Define a *dibasic* acid. 6. Explain the composition of the lead chamber crystals. 7. What is hydroxyl? 8. Write structural formulæ for several sulphur compounds. 9. Describe CS_2.

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